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STUDY OF THE TECHNICAL AND ECONOMIC FEASIBILITY OF A HYDROGENATION PROCESS FOR UTILIZATION OF WASTE RUBBER

HYDROCARBON RESEARCH, INC.

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By

R. H. Wolk and C. A. Battista
Research and Development Laboratory
Hydrocarbon Research, Inc.
Trenton, New Jersey

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Project Officer

Carlton C. Wiles
Solid Waste Research Laboratory
National Environmental Research Center
Cincinnati, Ohio 45268

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153

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

In an attempt to solve the problems involved in solid waste disposal, the technical and economic feasibility of a hydrogenation process for utilization of waste rubber is reported here.

A. W. Breidenbach, Ph.D.
Director
National Environmental
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16. Abstracts

The experimental program reported here was undertaken in an attempt to alleviate waste rubber and waste tire disposal problems. The program served to (1) demonstrate the technical feasibility of hydrogenation processing of waste, ground tire feeds; (2) evaluate the worth of liquid and solid products produced; and (3) develop a preliminary model of a commercial flow sheet. In the processing scheme, waste rubber was reacted with hydrogen in a special, proprietary, ebullated-bed reaction system to produce gas, oil, and solids. The work demonstrated that ground-up tires can be converted into naphtha, low sulfur fuel oil, and reusable carbon black by reaction in a hydrogenation system at elevated temperature and pressure. Data obtained in catalytic and non-catalytic reaction systems were compared. A preliminary design of a commercial plant that could convert 1,000 tons per day of ground up rubber was prepared and its costs were estimated.

17. Key Words and Document Analysis. 17a. Descriptors

*Rubber industry, *Rubber, *Wastes, *Waste disposal, Hydrogenation, Liquids, Solids, Models, Hydrogen, Gases, Oils, Naphthas, Carbon, Temperature, Pressure, Catalysis, Costs, Evaluation, Economic analysis, Industrial plants, Analyzing, Slurries, Elutriation

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III a

ABSTRACT

The work to date has demonstrated that ground up tires can be converted into naphtha, low sulfur fuel oil, and reusable carbon black by reaction in a hydrogenation system at elevated temperature and pressure. Comparisons of data obtained in catalytic and non-catalytic reaction systems indicate that the gross properties of the carbon black recovered from the two are the same and the 37 weight percent yield is essentially quantitative.

It is difficult to precisely assess the value of the carbon black since additional work is required on the separation of the black from the oil. Difficulties were encountered in dispersing black in rubber compounds after the black was separated from the oil, and in achieving a satisfactory cure rate with those rubber samples. Assuming that these problems are amenable to solution, based on satisfactory samples prepared at various times, the carbon produced by this process should be useful as a substitute for blacks selling in the $0.04 to $0.08 per pound range.

Significant differences exist, however, in the properties of naphtha and fuel oil products obtained from the two types of operation, which total about 60 weight percent yield. Additional catalytic hydrotreating of the naphtha and fuel oil was carried out and demonstrated that the sulfur content of these fractions could be lowered and their hydrogen content increased. The value of the liquid products as fuel is in the $3.00 to $4.00 per barrel range.

A preliminary design of a commercial plant to convert 1,000 tons per day of ground up rubber was prepared and estimated to cost $9.5 million. The major factors affecting the profitability of the plant were the cost of the ground rubber feed and the value of the carbon black product. A payout period of 3.9 years is projected for a plant receiving ground rubber at $30 per ton and selling carbon at $0.06 per pound. If these costs were changed to $20 and $0.08, respectively, the payout time would be reduced to 1.4 years. These calculations were based on 6% interest on working capital and 15 year straight line depreciation.

CONTENTS

		Page No.
	ABSTRACT	iv
I.	SUMMARY	1
II.	RECOMMENDATIONS FOR FUTURE WORK	3
III.	INTRODUCTION	5
	Scope of Work	5
	Waste Rubber Problems	6
	Waste Tire Disposal Problems	8
	H-Rubber Process	9
IV.	EXPERIMENTAL PROGRAM	13
	Introduction	13
	Feedstock Inspections	14
	Stirred Autoclave Experiments	27
	Catalytic Pilot Plant Operations	48
	Non-Catalytic Pilot Plant Operations	73
	General Discussion of Results	95
	Proposed Commercial Flow Sheet	98
V.	PRODUCT EVALUATIONS	105
	Introduction	105
	Results	105
	Discussion of Results	117
VI.	ECONOMIC CONSIDERATIONS OF THE H-RUBBER PROCESS	121
	Plant Location Concepts	121
	Plant Size	122
	Economic Analysis of a 1,000 TPSD H-Rubber Plant	122
	H-Rubber Plant Profitability	131

CONTENTS

	Page No.
APPENDIX	133
Analytical Test Development	133
Slurry Pumping Tests	137
Fiber Separation by Elutriation and Screening	138
REFERENCES	141

FIGURES

Figure No.	Title	Page No.
1	Conceptual H-Rubber Plant	10
2	Stirred Autoclave Tests - Effect of Temperature on Hydrocarbon Gas Make	46
3	Simplified Single-Stage H-Rubber Flow Sheet	51
4	H-Rubber Pressure Filtration Operation	54
5	Simplified Two-Stage H-Rubber Flow Sheet	56
6	Process Flow Diagram - Hydrogenation Section ------ 1,000 T/D Rubber	99
7	Effect of Carbon Value, Liquid Product Value and Ground Rubber Cost on Payout Period	132
8	Comparison: Standard DBP Number Versus DBP Number by HRI Titration	136

TABLES

Table No.	Title	Page No.
1	Summary of Rubber Consumption in Thousands of Tons	7
2	Feed Analyses: HRI 3184 -24 Mesh Ground Rubber Tires	16
3	Feed Analyses: HRI 3219 -24 Mesh Ground Rubber Tires	17
4	Feed Analyses: HRI 3221 -24 Mesh Ground Rubber Tires	18
5	Feed Analyses: HRI 3286 -24 Mesh Ground Rubber Tire Tread Peelings	19
6	Feed Analyses: HRI 3351 One-Quarter-Inch Ground Rubber Tires	20
7	Sieve Analyses: Ground Rubber Tires	22
8	Semi-Quantitative Emissions Spectrographic Analyses: Ash from Ground Rubber Tires	23
9	Analyses of Slurry Oils	24
10	Feedstocks - Autoclave Experiments	25
11	Feedstocks - Catalytic and Non-Catalytic Ebullated Pilot Plants	26
12	H-Rubber Autoclave Runs Summary	29
13	H-Rubber Autoclave Runs Summary	30
14	Autoclave Product Gas Yields	31
15	Autoclave Catalyst Comparison	36

TABLES

Table No.	Title	Page No.
16	Autoclave Product Oil ASTM Distillation	40
17	Autoclave Product Sulfur Distribution	41
18	Pseudo-DBP Numbers at Various Operating Conditions	45
19	Operating Program: Single-Stage Catalytic H-Rubber Runs	49
20	Operating Program: Two-Stage H-Rubber Runs	50
21	Catalytic Experiments - Liquid Product Inspections	61
22	Catalytic Pilot Plant Runs: Summary of Yields and Overall Material Balances	63
23	Operating Conditions - Run 144-156	66
24	Summary of Yields and Overall Material Balances -24 Mesh Ground Tread Peelings	68
25	Liquid Product Inspections - Run 144-156	70
26	Operating Program: Non-Catalytic Pilot Plant Operations	74
27	Experimental Material Balances and Yield Summary - Run 144-147	76
28	Experimental Material Balances and Yield Summary: Non-Catalytic Hydrogenation Operations - Run 144-149	78
29	Liquid Product Inspections - Run 144-149	79

TABLES

Table No.	Title	Page No.
30	Comparison of Actual to Theoretical Carbon Black Yields - Non-Catalytic Operations	80
31	Experimental Material Balances and Yield Summary - Non-Catalytic Operations - Run 144-150	83
32	Liquid Product Inspections - Run 144-150	84
33	Comparison of Actual to Theoretical Carbon Black Yields - Non-Catalytic Hydrogenation Operations	85
34	Sulfur Balances (Based on 100% Overall Material Balances) - Run 144-150	87
35	Summary of Inspections of H-Rubber Product Fractions - Run 144-154	89
36	Analysis of the 200-350°F Naphtha Fraction Non-Catalytic Hydrogenation Operations - Run 144-154	90
37	Summary of Yields: Non-Catalytic Hydrogenation Operations on -24 Mesh Ground Tires - Run 144-154	91
38	Summary of Hydrotreating Results of H-Rubber Product Fractions	93
39	Summary of Hydrotreating Results of H-Rubber Naphtha	94
40	Hydrogenation Plant Yields (1000 T/D Rubber)	102
41	Hydrogenation Plant Material Balances (1000 T/D Rubber)	103

TABLES

Table No.	Title	Page No.
42	Evaluation of Experimentally Produced Carbon Blacks in Natural Rubber Compounds - Standard Test Recipe	107
43	SBR Compounds: Standard Test Recipe	110
44	SBR Compounds: Modified Test Recipe	113
45	Evaluation of Modified Carbon Blacks in SBR Compounds	115
46	Comparison of H-Rubber Oil and Sundex 790 Aromatic Oil in SBR Compounds	116
47	EPDM Hose Compounds	118
48	Potential Locations for H-Rubber Plants	123
49	Economic Summary for 1000 TPSD Plant	124
50	1,000 Ton/Day H-Rubber Plant Estimated Capital Investment	128
51	1,000 Ton/Day H-Rubber Plant: Summary of Capital Investment, Products, Raw Materials and Utilities	129
52	1,000 Ton/Day H-Rubber Plant: Operating and Management Payroll	130

I. SUMMARY

The most significant conclusion resulting from the study is that ground rubber tires can be converted in a hydrogenation reactor operating at conventional petroleum industry conditions of temperatures ranging from 660°F to 850°F and hydrogen partial pressures of 500 to 2,000 psig to a product slate of fuel gas, naphtha, gas oil, and carbon black. It was found that the reaction could be carried out either in the presence or absence of commercially available hydrotreating catalysts. No gross differences were found in the carbon blacks recovered in either case, but significant differences were found in the sulfur and hydrogen content of the liquid products. The yield of carbon and other inorganic compounds was found to be quantitative with respect to the original composition of the tires. No additional carbon-containing material, such as coke, was produced in the process.

No major operating difficulties were encountered in continuous ebullating bed, non-catalytic operations in a 0.614-inch inside diameter reactor on -24 mesh particles obtained from grinding whole tires. Catalytic operation in the same pilot plant on tire tread peelings, which were essentially free of glass fibers, was also successful. However, severe operating difficulties were encountered in the same unit when operating with a catalyst bed and processing ground tires containing glass fibers. It is felt that these difficulties were, for the most part, due to the unreactive glass fibers matting together, which caused plugs to form in the reactor. This difficulty was not encountered in the stirred autoclave unit in which the initial screening studies were done and it is anticipated that it would not occur in larger scale pilot plants or in commercial sized units.

Carbon black and oil produced in this work were evaluated to ascertain the potential of these materials for reuse in the manufacture of new tires. A variety of rubber compounds were manufactured using carbon recovered from both catalytic and non-catalytic operations and oil from the non-catalytic operation. Physical tests of the compounds made from the carbon characteristically showed low modulus (amount of pull) at 300 percent

elongation and slow cure rate with one exception. In that case, a blend containing equal amounts of virgin carbon and recovered carbon was used, along with recovered oil, to produce a compound having satisfactory properties.

A small number of compounds were made with carbons that were thermally treated to remove surface contaminants or that had their pH adjusted. Improved results were obtained from these treatments.

Overall economics are primarily dependent on the cost of collecting and grinding the used tires, and on the value of the carbon black product. With a total ground rubber cost of $30 per ton, including collecting and grinding, a plant payout period of 3.92 years is obtained with carbon worth $0.06 per pound. This is based on 6% interest and 15 year straight line depreciation.

If the rubber cost dropped to $20 per ton, the plant payout time would drop to 2.4 years. Alternately, if the carbon value rose from $0.06 to $0.07 per pound, the plant payout period would drop to 2.4 years for $30 per ton rubber and 1.7 years for $20 per ton rubber.

II. RECOMMENDATIONS FOR FUTURE WORK

The work that has been carried out has demonstrated that hydrogenation is a technically feasible means of eliminating waste rubber tires. Additional experimental work and product evaluation studies are required to optimize the system so that it is a commercially viable process. These are proposed below:

1. Since a reduction in rubber grinding costs would have a major effect in improving overall economics, investigations should be carried out on how to feed one-quarter-inch or larger pieces of ground rubber into the system.

2. Longer pilot plant runs in both the catalytic and non-catalytic reactor systems are required to determine if important trends occur in the primary and secondary reactions which would affect product quality.

3. More product analysis work is needed to differentiate between catalytically and non-catalytically produced carbon and oil products so that the overall economics for each scheme may be better defined.

4. Since the various separation techniques used in this program to separate carbon and oil seemed to affect carbon product quality, additional studies are required to improve this step.

5. Extensive hydrotreating studies on the naphtha and gas oil products are required to determine optimum conditions for upgrading these materials.

6. Process engineering studies should be made so that the most economical plant flow sheet can be developed.

7. Additional rubber compounding tests should be carried out with separated product carbon blacks, treated product carbon blacks, and unseparated oil/carbon black mixtures so that a precise value of these materials can be arrived at.

III. INTRODUCTION

Hydrocarbon Research, Inc. (HRI) has investigated, under Contract No. 68-03-0050, the "Study of the Technical and Economic Feasibility of a Hydrogenation Process for Utilization of Waste Rubber" for the Solid Waste Research Laboratory, National Environmental Research Center - Cincinnati, Office of Research and Monitoring, U.S. Environmental Protection Agency.

SCOPE OF WORK

Phase I of the program served to (1) demonstrate the technical feasibility of hydrogenation processing of waste ground tire feeds, (2) evaluate the worth of liquid and solid products produced, and (3) develop a preliminary model of a commercial flow sheet. In the processing scheme, waste rubber was reacted with hydrogen in a special, proprietary, ebullated bed reaction system to produce gas, oil, and solids. Essentially, the hydrogenation technology used was similar to that developed previously by HRI for processing coal and petroleum residual feedstocks[1,2,3,4,5,6].

The basic practicality of the processing scheme is assured by (1) the successful large-scale pilot plant demonstration of coal liquefaction using hydrogenation techniques (H-Coal)[7,8], and (2) successful commercial plant operation of the HRI hydrogenation process using residual feeds from petroleum sources (H-Oil)[9,10]. This latter development has resulted in large-scale plant applications of the basic technology which can be applied to waste rubber.

Uniroyal Chemical Company acted as a subcontractor to HRI and provided technical skills based on its background, capabilities, and experience in utilizing and manufacturing a wide array of

rubber products and reclaiming waste rubber tires. Uniroyal carried out product evaluations on the carbon and oil produced to assess their potential for reuse in tire manufacturing and provided costs for grinding tires.

WASTE RUBBER PROBLEMS

The United States rubber industry, in satisfying customer and industrial demands for a variety of rubber products, consumed 5.2-billion pounds of natural and synthetic elastomers in 1969. Table 1 provides a breakdown of the chemical classes of elastomers used by manufacturers and indicates an overall growth in elastomer consumption of 30 percent in the period 1969 to 1975[11]. As indicated, styrene butadiene rubber (SBR), primarily used for tire manufacturing, represents the largest single elastomer type used by the rubber industry.

Tires and related automotive uses consume about 65 percent of the elastomer production in the United States[12]. Tire manufacturers have developed a product that is reliable and dependable for about 50,000 miles of travel service, stable in the face of severe changes in weather conditions, and available at retail outlets for a price of about $1 per pound. Many materials other than rubber are used when a manufacturer makes tires. Elastomers are compounded with inorganic materials, including carbon black, sulfur, zinc oxide, clay fillers, calcium and magnesium carbonates and silicates, as well as a variety of inorganic pigment materials. Organic additives include accelerators, plasticizers, softeners and extender oils, and various modifiers and antioxidants. The organic and inorganic additives modify the properties of synthetic and natural elastomers in order to obtain characteristics desired in the final product. In 1969, about 3-billion pounds of the compounds listed above were used by the rubber industry.

In addition to the organic and inorganic chemical modifying agents, considerable quantities of fibers are consumed in the manufacture of rubber products. About 600-million pounds of tire cord (rayon, nylon, polyester, and glass) were consumed in

SUMMARY OF RUBBER CONSUMPTION IN THOUSANDS OF TONS

ELASTOMER TYPE	1969	1975
SBR	1300	1400
Polybutadiene	271	465
Neoprene	120	160
Butyl	92	113
Polyisoprene	85	200
Nitrile	65	84
Ethylene-Propylene	44	225
Other	26	42
Total Synthetic	2001	2689
Natural Rubber	588	685
Total Consumption	2589	3374

Source: Chemical and Engineering News, September 7, 1970

TABLE 1

tire manufacture in 1969[12]. In manufacturing rubber products, some 5- to 6-billion pounds of natural and synthetic elastomers and 3- to 4-billion pounds of organic and inorganic chemicals and other materials were consumed.

Reuse of tires after retreading appears to have a very limited potential impact on the problem of reducing the amount of waste tires. In a recent EPA report[13], it was pointed out that, in 1968, 69.1 percent of used passenger tires ended up as waste, 20.8 percent were retreaded, and 9.1 percent were reclaimed. On the basis of an estimated production of 220-million passenger tires in 1974, it was anticipated that 72.3 percent would go to waste, 19.2 percent would be retreaded, and 7.3 percent reclaimed. The reasons for the low percentage of retreading are related to poor consumer acceptance of the concept of retreaded tires being as good as new tires, competition with some lower quality, lower priced lines of new tires, and excessive carcass abuse to the majority of used tires.

WASTE TIRE DISPOSAL PROBLEM

In 1969, the United States rubber industry produced over 220-million units of tires for passenger cars, trucks, airplanes, and farm and industrial vehicles[11]. The tire is used until it is worn out and is then discarded. This tire carcass represents an eyesore and a solid waste pollutant because of the excellent resistance to degradation built into the product by the manufacturer. The presence of oil (used to "extend" the rubber) and sulfur in high concentrations in the tire cause it to produce a smoky flame and noxious decomposition products (SO_2) when burned in open air. Because of this, pollution legislation forbids burning tires. Tires also have a tendency to reappear on the surface after being buried in landfill operations and represent a breeding place for rodents and insects.

Incineration of tires can result in damage to the municipal incinerator and are usually not accepted for that reason. In the incinerator, a tire melts into a sticky mass which sinks to the bottom and adheres to the grate. The high temperature resulting from the combustion of the melted tire on the grate can damage the grate by causing it to warp.

H-RUBBER PROCESS

The basic premise for the experimental study described in this report was to develop a process to dispose of tires in a way that would enable the major constituents of the original tire to be economically recovered in a useful form. Ebullated bed hydrogenation was selected as the best technique for this purpose because it was thought that:

1. The carbon contained in the original tire will not react with hydrogen and should be recoverable with its original properties intact.

2. The rubber and cord materials are easily converted into relatively low boiling petroleum-type fractions and gas as a result of hydrogenation and cracking reactions.

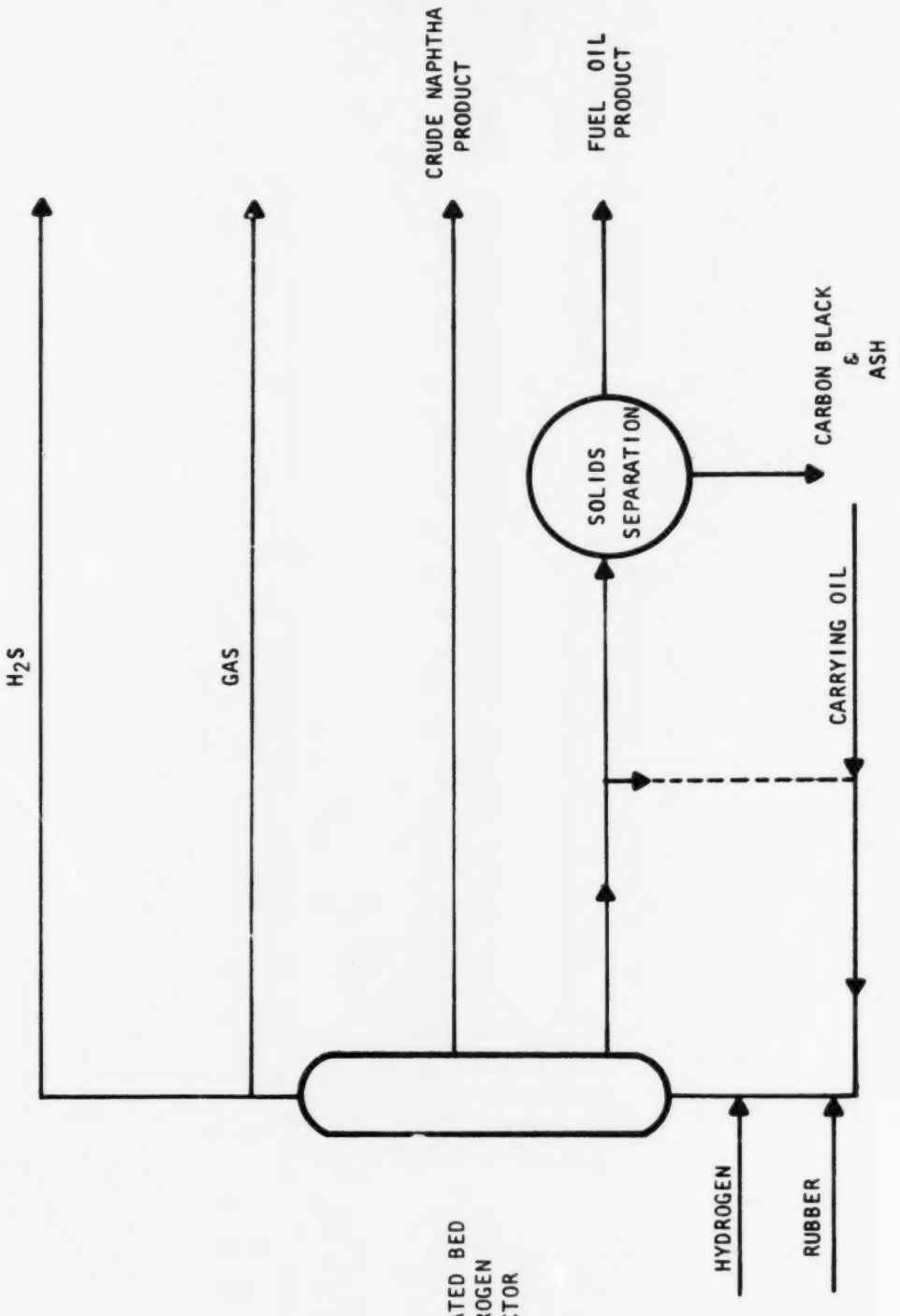
3. The oil used to extend the rubber in the tire manufacturing process may be recovered with only minor changes and have potential for reuse.

4. Other solids, such as clay fillers, glass fibers, and inorganic chemicals, such as zinc oxide, which are present in the feed in finely divided form, pass through the reactor system without change.

A conceptual flow diagram of the process, which will be referred to as the H-Rubber process in the remainder of the report, is shown in Figure 1. In the process, tires from storage are shredded and reduced in size to permit charging a slurry of rubber and oil to the reactor system. The slurrying oil may be generated from the rubber conversion or, alternatively, extraneous oil could be used.

Separation of carbon from a mixed heavy oil and carbon product stream is required. Part of the oil obtained from this stream must be recycled to slurry the ground tires. The net heavy oil produced along with the light oil (naphtha) and gas can be sold

FIGURE 1



CONCEPTUAL H-RUBBER PLANT

as fuel. Preferably the heavy oil could be recycled back into the tire manufacturing operation.

Significant hydrogenation process economics could be realized by locating an H-Rubber plant immediately adjacent to a refinery. For example, the extraneous oil stream can be an aromatic gas oil such as that derived from catalytic cracking units operating in most petroleum refineries. Hydrogen consumed in processing 1,000-tons-per-day of rubber would correspond to about 3- to 4-million standard-cubic-feet-per-day. There are a number of refineries in this country which have this quantity of hydrogen available from (1) catalytic reforming, or (2) surplus hydrogen from existing manufacturing facilities which is not being completely used. This amount of hydrogen also could represent a small amount of incremental capacity for a larger hydrogen plant which could be installed (conventionally, hydrogen plants of the order of 100-million standard-cubic-feet-per-day capacity are installed in refineries).

In addition, the amount of offsites required to provide electrical power, steam, water, pollution control facilities for waste water, liquid product upgrading and gas cleanup facilities could be substantially reduced by integrating this operation with a large refinery. These services could be provided on an incremental cost basis which is less expensive. Major oil refineries in the United States range in size between 100,000 and 400,000 barrels per day of crude oil capacity. One 1,000 ton per day H-Rubber plant would produce on the order of 3,000 barrels per day of liquid products. This amount represents a small proportion of a refinery's total throughput and might be handled without expansion of existing facilities.

IV. EXPERIMENTAL PROGRAM

INTRODUCTION

It was decided to use a one-liter magnetically stirred batch autoclave to carry out the initial studies on the reaction of ground tires and hydrogen in the presence of a particulate hydrogenation catalyst and a hydrocarbon slurry oil. This decision was reached on the basis that the system simulated to a reasonable degree an ebullated bed reactor which was used for the continuous pilot plant studies carried out later in the program. It had the additional advantage of producing data quickly and at low cost, since the experiments were short in duration and the unit could be rapidly turned around between experiments.

The objective of this series of experiments was to determine the range of operating conditions that would satisfactorily react the rubber so that a carbon black and ash could be easily separated from the reaction products. In addition, it was anticipated that the quality of the carbon would vary as a function of operating conditions and type of catalyst used. The levels of the variables investigated varied over the ranges listed below:

Temperature	460-850°F
Pressure	500-2,000 psig
Catalysts	None, four cobalt molybdate on alumina, one nickel molybdate on alumina
Time at Temperature	0-6 Hours
Slurry Oils	None, anthracene oil, hydrogenated anthracene oil, tetralin

It was hoped that the results of these experiments would enable us to reduce the amount of experimental work required in the continuous ebullated bed pilot plant units.

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The continuous catalytic H-Rubber runs were made to determine long-term process operability, provide data for process material balances, and study the yield and quality of gaseous and liquid products produced. Operating conditions for the initial runs were selected on the basis of information developed during the stirred autoclave studies. A total of eleven runs were made. Eight of these were made in a single-stage unit.

Since serious operating difficulties were encountered in the early catalytic runs, three ebullated bed runs were made to investigate the effect of a two-stage reactor system on operability and product quality. The first stage reaction was non-catalytic to decompose the rubber and "spring" the carbon black. It was hoped that the decomposition of the rubber would aid ebullation in the second, catalytic stage. As an added benefit, it was anticipated that the catalytic hydrogenation in the second stage would produce better quality liquid and gas products.

A series of four non-catalytic, pilot plant runs were made to explore the concept of non-catalytic hydrogenation to free carbon black from ground rubber tires. Initial experimental work in the stirred autoclave system had indicated that the carbon could be released. Continuous pilot plant work was needed to demonstrate long-term process operability, provide data for process material balances, and study the yield and quality of gaseous and liquid products produced.

FEEDSTOCK INSPECTIONS

General

The feedstocks used for both the initial batch experiments in the stirred autoclave reactor and the continuous ebullated bed operation consisted of ground rubber tires, slurry oil, and hydrogen.

Four shipments of -24 mesh ground, rubber tire feedstock were received from Uniroyal Chemical. The first was one 50-pound bag (HRI 3184)*, which was used in the stirred autoclave runs. The second shipment (HRI 3219) consisted of two 50-pound bags, which contained material identical to that received in the third shipment of a total of 2,000 pounds (HRI 3221). The fourth shipment (HRI 3286) was one 50-pound bag of ground tire tread peelings.

One shipment of ground tire cord fibers (HRI 3220), containing a small percentage of rubber, was received from Uniroyal. No analyses are available on the fibers which would indicate their original type.

In addition, one shipment of one-quarter-inch ground rubber, including fibers (HRI 3351), was received.

Tables 2 to 6 list the proximate and ultimate analyses of the ground rubber feeds.

Rubber Feedstock

The -24 mesh ground, rubber tire feedstock was from a random selection of used tires which were ground by Uniroyal Chemical as part of their rubber reclaiming program. All but two to four percent of the fibers were removed by air elutriation. No componential breakdown on the fiber species or on the synthetic rubber concentration contained in the feedstock is available. The tires, as previously mentioned, were a random selection of used tires and, therefore, contained different types of

* All samples received by HRI, whether catalyst, oils, or solids, are given an HRI number upon receipt. This number is then used to identify that particular sample in all further test work.

TABLE 2

FEED ANALYSES

HRI 3184

-24 MESH GROUND RUBBER TIRES

	As Received	Dry Basis
PROXIMATE ANALYSIS		
% Moisture	0.62	----
% Ash	5.31	5.34
% Volatile	63.81	64.21
% Fixed Carbon	30.26	30.45
	100.00	100.00
ULTIMATE ANALYSIS		
% Moisture	0.62	----
% Carbon	82.50	83.01
% Hydrogen Organics	7.22	7.26
% Nitrogen	0.64	0.64
% Sulfur	1.44	1.45
% Ash	5.31	5.34
% O_2 by Difference	2.27 (4.59)[1]	2.30
	100.00	100.00

1. % O_2 by Unterzaucher Method

TABLE 3

FEED ANALYSES

HRI 3219

-24 MESH GROUND RUBBER TIRES

	Bag 1		Bag 2	
	As Received	Dry Basis	As Received	Dry Basis
PROXIMATE ANALYSIS				
% Moisture	0.22	----	0.22	----
% Ash	5.56	5.57	5.52	5.53
% Volatile	63.77	63.91	63.99	64.13
% Fixed Carbon	30.45	30.52	30.27	30.34
	100.00	100.00	100.00	100.00
ULTIMATE ANALYSIS				
% Moisture	0.22	----	0.22	----
% Carbon	83.20	83.38	84.00	84.18
% Hydrogen Organics	7.35	7.37	7.50	7.52
% Nitrogen	0.28	0.28	0.28	0.28
% Sulfur	1.65	1.65	1.65	1.65
% Ash	5.56	5.57	5.52	5.53
% O_2 by Difference	1.74	1.75	0.83	0.84
	100.00	100.00	100.00	100.00

TABLE 4

FEED ANALYSES

HRI 3221

-24 MESH GROUND RUBBER TIRES

	As Received	Dry Basis
PROXIMATE ANALYIS		
% Moisture	0.56	----
% Ash	5.51	5.54
% Volatile	63.29	63.65
% Fixed Carbon	30.64	30.81
	100.00	100.00
ULTIMATE ANALYSIS		
% Moisture	0.56	----
% Carbon	82.80	83.26
% Hydrogen Organics	7.30	7.34
% Nitrogen	0.39	0.39
% Sulfur	1.43	1.44
% Ash	5.51	5.54
% O_2 by Difference	2.01 (2.31/3.27)[1]	2.03
	100.00	100.00

1. Two separate % O_2 determinations by Unterzaucher Method

TABLE 5

FEED ANALYSES

HRI 3286

-24 MESH GROUND RUBBER TIRE TREAD PEELINGS

	As Received	Dry Basis
PROXIMATE ANALYSIS		
% Moisture	0.45	----
% Ash	5.67	5.70
% Volatile	64.57	64.86
% Fixed Carbon	29.31	29.44
	100.00	100.00
ULTIMATE ANALYSIS		
% Moisture	0.45	----
% Carbon	82.50	82.82
% Hydrogen Organics	7.49	7.52
% Nitrogen	0.27	0.27
% Sulfur	1.42	1.43
% Ash	5.67	5.70
% O_2 by Difference	2.20	2.21
	100.00	100.00

TABLE 6

FEED ANALYSES

HRI 3351

ONE-QUARTER-INCH GROUND RUBBER TIRES

	As Received	Dry Basis
PROXIMATE ANALYSIS		
% Moisture	1.04	----
% Ash	6.36	6.43
% Volatile	64.23	64.90
% Fixed Carbon	28.37	28.67
	100.00	100.00

Ultimate Analysis is not available for this feed because the particle size of the individual pieces is too large for the analytical procedure used.

cord; including fiber glass, nylon, rayon, and polyester; and different types of rubber. Most of the ground tire (approximately 86%) in the -24 mesh sample was in the particle size range of 20/50 U.S. mesh. Table 7 gives detailed sieve analyses.

Table 8 lists semi-quantitative metals analyses of the ash from the rubber. These spectrographic analyses indicated that the major metal components are zinc and silicon.

Slurry Oil

The slurry oil used for most of the autoclave and some of the ebullated bed runs was anthracene oil, which is derived from coal tar. It was felt that this material would provide a molecular type and boiling range which would be close to that ultimately obtained by the hydrogenation of the ground rubber tires. However, for the ebullated bed runs, hydrogenated anthracene oil was used in place of regular anthracene oil because it was felt that the hydrogen content of the ring structure molecules was lower than the product oil would be from the rubber. During one ebullated bed run, a Kuwait light gas oil was used as a slurry oil to evaluate an oil with a much lower aromatic content than anthracene oil.

Analytical inspections of the oils are given in Table 9. Tables 10 and 11 list the various rubber feedstocks and the corresponding runs in the H-Rubber program in which they were used for the stirred autoclave and ebullated bed runs, respectively.

TABLE 7

SIEVE ANALYES

GROUND RUBBER TIRES

HRI Number	3184	3219 Bag #1	3219 Bag #2	3221	3286
U.S. Standard Sieve Number					
+20, W %	5.18			1.62	0.00
20/30	37.15	51.03	55.95	54.67	55.77
30/40	26.51				
40/50	14.26	26.64	23.27	25.74	19.58
50/60	7.83	12.76	11.81		
60/70		4.31	4.43	8.21	7.70
70/80	4.15	3.53	2.89		6.36
80/100		1.40	1.18	5.48	3.01
100/140	2.53	0.34	0.47	2.93	1.45
140/200	0.82			1.36	
200/270	0.40				
270/325	0.14				
325/PAN	1.03				

TABLE 8

SEMI-QUANTITATIVE EMISSIONS SPECTROGRAPHIC ANALYSES

ASH FROM GROUND RUBBER TIRES

HRI Number	3184	3219 Bag #1	3219 Bag #2	3221	3286	3351
	Analyses (1)					
ELEMENT						
Aluminum	3.0	5.0	5.0	3.0	5.0	10.0
Barium	0.2	0.2	0.3	0.2	0.1	0.3
Beryllium	----	----	----	----	N.D.	N.D.
Boron	0.1	0.3	0.2	0.2	0.003	0.3
Cadmium	0.02	0.02	0.02	----	----	----
Calcium	3.0	4.0	4.0	3.0	3.0	5.0
Chromium	0.03	0.03	0.03	0.04	0.3	0.07
Cobalt	0.01	0.01	N.D.	N.D.	0.01	N.D.
Copper	0.03	0.03	0.03	0.03	0.2	0.1
Gallium	0.01	0.01	0.01	0.005	N.D.	0.01
Germanium	----	----	----	N.D.	----	----
Iron	1.0	1.0	1.0	1.0	3.0	7.0
Lead	0.3	0.2	0.2	0.2	0.2	0.3
Magnesium	2.0	1.0	1.0	2.0	7.0	3.0
Manganese	0.03	0.03	0.03	0.03	0.1	0.08
Molybdenum	0.01	----	----	N.D.	----	----
Niobium	0.02	0.02	0.02	0.02	----	----
Nickel	0.1	0.05	0.03	0.03	0.3	0.2
Phosphorous	0.1	0.1	0.1	0.2	0.3	0.3
Silicon	10.0	10.0	10.0	10.0	10.0	Maj.
Silver	0.003	----	----	----	----	----
Strontium	0.03	0.03	0.05	0.05	0.01	0.03
Tin	0.03	0.03	0.03	0.03	0.05	0.03
Titanium	3.0	5.0	5.0	5.0	0.8	5.0
Vanadium	0.01	0.01	0.01	0.01	0.01	0.02
Zinc	10.0	Maj.	Maj.	Maj.	Maj.	Maj.
Zirconium	0.02	0.03	0.03	0.02	0.003	0.01
Sodium					Int.	Int.

N.D. = Not Detected
Maj. = Major Constituent
Int. = Interference

(1) The above results are order of magnitude only, not actual percentages, for comparison within these specific analyses.

TABLE 9

ANALYSES OF SLURRY OILS

	Kuwait Gas Oil	Hydrogenated Anthracene Oil	Regular Anthracene Oil
HRI Number	3051	L-279 (similar to L-320)	3116 (Similar to 2998)
Gravity, °API	32.3	-1.1	-7.3
Sulfur, W %	1.89	0.13	0.87
ASTM Distillation			
IBP, °F	508	436	496
5, V %	522	---	535
10, V %	535	473	550
20, V %	556	516	600
30, V %	575	572	632
40, V %	590	586	---
50, V %	605	509	---
60, V %	616	630	---
70, V %	630	660	---
80, V %	642	696	---
90/95, V %	658/665	747/768	---
FBP	675	845	---
Recovered	97	98	40
Residue	2	2	59
Loss	1	0	1
Volume % off at 600°F	46	48	20
" " " " 650°F	86	67	38

TABLE 10

FEEDSTOCKS - AUTOCLAVE EXPERIMENTS

Run	Rubber, HRI No.	Slurry Oil, HRI No.
193-140	3184	2998
193-144	3184	2998
193-145	3184	2998
193-146	3184	2998
193-147	3184	2998
193-148	3184	2998
193-149	3184	3116
193-150	3184	3116
193-151	3184	3116
193-152	3184	LC-135 (Tetralin)
193-156	3184	3116
193-157	3184	3116
193-158	3184	----
193-159	3184	3116
193-160	3184	3116
193-161	3184	3116
193-162	----	3116
193-163	3184	3116
193-164	3220 (Fibers)	3116
193-165	3184	3116
193-166-1	3184	3116
193-166-2	Feedstock - Product from 193-166-1	
193-167	3351	L-320
193-168	3351	L-320

TABLE 11

FEEDSTOCKS - CATALYTIC AND NON CATALYTIC EBULLATED PILOT PLANTS

Run	Rubber, HRI No.	Slurry Oil HRI No.
144-144	3219 (As Received)	L-279
144-145	3219 (As Received)	L-279
144-146	3219 (-36 Mesh)	L-279
144-147	3219 (-36 Mesh)	L-279
144-148	3219 (-36 Mesh)	L-279
144-149	3219/3221 (-36 Mesh)	L-279
144-150-1/2/3	3221 (-36 Mesh)	L-279
144-150-4	3221 (As Received)	L-279
144-150-5	3221 (As Received)	3051
144-151	3221 (As Received)	L-279
144-152	3221 (As Received)	L-279
144-153	3221 (-36 Mesh; Low Fibers)	L-279
144-154	3221 (As Received)	L-279
144-156	3286 (Tread Peelings)	L-279
177-72	3221 (-36 Mesh)	L-279
177-73	3221 (-50 Mesh)	L-279

STIRRED AUTOCLAVE EXPERIMENTS

Experimental Procedures

The initial experimental work was carried out in a stirred autoclave reactor designated as Unit 193. The specific unit used was an Autoclave Engineers one-liter Magnadrive Autoclave.

Ground tires, oil, d catalyst were weighed and charged to the autoclave reactor. top flange, with its stirrer, was bolted on and the system was purged and pressure tested at 3,000 psig with hydrogen. The reactor hydrogen pressure was set with a back-pressure regulator and the vent gas flow rate was measured using a wet test meter. The stirrer speed was then set at the desired rpm.

The reactor temperatures were slowly raised using a West Guardsman temperature controller (Model JSB). One reactor internal temperature and one reactor skin temperature were recorded. When the internal temperature was lined out at the desired reaction temperature, the run was officially begun. Usually, it took about one hour to reach a reaction temperature of 750°F.

During the run, the vent gas was measured and sampled. At the end of the run (a predetermined length of time), heats on the reactor were shut off and the reactor was allowed to cool and reach its own equilibrium pressure.

At 100°F, the unit was depressurized into a gas holding drum in which the product gas displaced water. The drum was refilled with water displacing the product gas through a glass sampling vessel and through a wet test meter for a flash gas volume measurement.

The top reactor flange was opened and the stirrer was removed. Visual examination of the product in the reactor vessel was made. The bottom plug on the autoclave reactor was knocked out

and the product was drained into a collecting vessel. The inside of the reactor was washed with benzene and the wash liquid was saved in another vessel. The benzene was later gently distilled off to get a weight on the residue for a material balance.

The solids were separated from the oil product in the Analytical Laboratory by washing the total liquid-solids product with benzene through a 60 mesh screen to remove the catalyst. A benzene extraction was done on the remaining oil-carbon black product to separate out the carbon black. The benzene-oil mixture was then separated by distillation. A more detailed discussion of the procedure is presented in the Appendix.

The final products consisted of catalyst, carbon black plus inorganics, oil, vent gas, and flash gas. Analyses of each of these products were made.

Results

The operating conditions, product yields, and material balances for all of the stirred autoclave runs are summarized in Tables 12 and 13. Gas yields from these runs are summarized in Table 14. These yields were expressed in grams instead of expressing them as weight percent on feed, since a large proportion of the gas comes from the ground rubber tires and a small proportion from the slurry oil.

Initial Runs: Analytical data for the initial run (193-139) was not worked up because of an electrical short circuit that developed in the autoclave heater system which made it necessary to cool down the reactor before reaching the desired operating temperature. The second run (193-140) was made at conditions that were used in the pre-proposal experiments. The analytical data obtained in this run indicated that the carbon, which amounts to about 35 percent of the rubber fed to the autoclave, could be obtained almost quantitatively as our pre-proposal experiments had indicated.

H-RUBBER AUTOCLAVE RUNS SUMMARY

Run 193-	Temp. °F	Pres. psig	Stirrer rpm	Catalyst	Catalyst Type	HRI No.	Time to Reach Run Temp. (Hrs)	Time at Temp.	Charge, Gms.			Products, Gms.					Material Bal.	
									Rubber	Anthracene Oil	Cat.	Oil	Cat.	Carbon Black + Inorgs.	% Catalyst in Carbon + Inorgs.	Gas	Pilot Plant	Anal. Lab
140	850	1000	750	1/32" Ketjen	CoMo on Alumina	2280	1.5	Held at 850°F for 1 hour	67.0	136.0	10.0	114.2	9.5	20.0	9.0	31.8	104	82
144	660	1000	200	1/32" Ketjen	CoMo on Alumina	2280	6.0	Shut down on reaching 660°F	67.0	133.1	10.0	164.0	8.7	23.0		3.7	93	95
145	750	1000	200	1/32" Ketjen	CoMo on Alumina	2280	1.5	Shut down on reaching 750°F	67.0	135.3	10.0	171.0	11.9	21.2	Negl.	1.4	91	96
146	750	500	200	1/32" Ketjen	CoMo on Alumina	2280	1.0	Shut down on reaching 750°F	67.0	132.9	10.0	168.3	12.8	23.3		1.2	93	97
147	460	1000	200	1/32" Ketjen	CoMo on Alumina	2280	1.3	Held at 460°F for 1 hour	67.0	134.0	10.0					1.4	81	
148	750	1000	200	1/32" Ketjen	CoMo on Alumina	2280	1.5	Held at 750°F for 1 hour	67.0	132.4	10.0	177.3	12.3	22.6	Negl.	4.1	92	101
149	750	1000	200	HDS-3B	NiMo on Alumina	2604	1.3	Held at 750°F for 1 hour	67.0	133.0	10.0	161.3	11.3	22.0		3.6	98	93
150	750	1000	200	1/32" HDS-1441	CoMo on Alumina	2959	1.0	Held at 750°F for 1 hour	67.0	132.6	10.0	158.3	14.7	19.4		4.2	100	92
151	750	1000	200	1/32" HDS-1442B	CoMo on Alumina	3071	1.0	Held at 750°F for 1 hour	67.0	134.6	10.0	175.3	13.0	23.1		6.4	101	102
152	750	1000	200	1/32" Ketjen	CoMo on Alumina	2280	1.2	Held at 750°F for 1 hour	67.0	133.0*	10.0	159.0	11.2	23.1		4.0	97	92

* Tetrahydronaphthalene (tetralin) used in place of anthracene.

TABLE 12

H-RUBBER AUTOCLAVE RUNS SUMMARY

Run 193-	Temp. °F	Pres. psig	Stirrer rpm	Catalyst	Catalyst Type	HRI No.	Time to Reach Run Temp. (Hrs)	Time at Temp.	Charge, Gms.			Products, Gms.					Material Bal.	
									Rubber	Anthracene Oil	Cat.	Oil	Cat.	Carbon Black + Inorgs.	% Catalyst in Carbon + Inorgs.	Gas	Pilot Plant	Anal. Lab
156	750	1000	200	None	--------	----	1.3	Held at 750°F for 1 hour	67.0	133.1	0.0	152.0	----	23.8		4.6	100	90
157	750	1000(N_2)	200	None	--------	----	1.3	Held at 750°F for 1 hour	67.0	133.5	0.0	239.0	----	24.8		9.4	102	136
158	750	1000	200	1/32" Ketjen	CoMo on Alumina	2280	1.0	Held at 750°F for 1 hour	200.0	-----	10.0	146.0	12.4	65.1		13.6	99	113
159	750	1000	200	1/32" Ketjen	CoMo on Alumina	2280	1.2	Held at 750°F for 1 hour	134.0	265.9	20.0	307.0	24.3	48.7		7.4	100	92
160	800	1000	200	1/32" HDS-1441	CoMo on Alumina	2959	1.5	Held at 800°F for 1 hour	134.0	265.8	20.0	364.0	28.2	55.0		13.4	101	109
161	850	1000	200	1/32" HDS-1441	CoMo on Alumina	2959	1.5	Held at 850°F for 1 hour	134.0	267.0	20.0	292.0	28.4	52.6		27.8	102	95
162	750	1000	200	1/32" HDS-1441	CoMo on Alumina	2959	1.3	Held at 750°F for 1 hour	0.0	133.0	10.0	-----	11.5	----		1.4	96	-
163	750	1000	200	1/16" Nalco 471	CoMo on Alumina	2308	1.5	Held at 750°F for 1 hour	134.0	265.0	20.0	333.0	23.8	46.9		5.9	99	98
165	750	2000	200	1/32" HDS-1441	CoMo on Alumina	2959	2.0	Held at 750°F for 1 hour	67.0	133.0	10.0	205.0	11.2	22.8		3.4	99	115
166-1	750	1000	200	None	-------	----	1.5	Held at 750°F for 1 hour	67.0	133.0	----	-----	----	----		---	--	--
166-2*	750	1000	200	1/32" HDS-1441	CoMo on Alumina	2959	1.5	Held at 750°F for 1 hour	----	-----	10.0	140.0	13.0	29.1		---	--	--
167	850	1000	200	None	-------	----	1.5	Held at 850°F for 1 hour	134.0	366.0	----	395.0	----	44.6		16.2	96	91
168	850	1000	200	None	-------	----	1.5	Held at 850°F for 1 hour	134.0	266.0	----	297.0	----	47.7		22.2	101	92

* Liquid product from 193-166-1 is the charge for Run 193-166-2.

TABLE 13

AUTOCLAVE PRODUCT GAS YIELDS

Run	193- 140	144	145	146	147	148	149	150	151	152	156	157	158	159	160	161	162	163	165	167	168
Gas Volume, Standard Cubic Feet	5.60	6.52	2.21	2.07	4.62	4.08	3.34	3.49	2.92	3.08	2.32	2.05	3.20	2.46	2.24	2.23	3.52	3.40	4.74	1.23	1.43
Total Hydrocarbon Gas Weight, C_1-C_6, Gms.	31.75	3.72	0.80	0.51	0.98	3.06	3.03	3.0	4.64	2.96	2.98	3.67	10.13	4.67	9.62	23.24	1.23	4.01	2.89	16.2	22.2
Gas Yields, Gms.																					
CH_4	8.88	0.12	0.08	0.05	0.02	0.45	0.52	0.46	0.92	0.56	0.32	0 26	1.75	0.59	2.81	6.38	0.18	0.69	0.37	1.16	3.84
C_2H_4	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
C_2H_6	7.40	----	0.10	0.03	0.04	0.25	0.43	0.40	0.78	0.50	0.32	0.28	1.59	0.53	2.14	6.54	0.19	0.55	0.37	3.18	3.52
C_3H_6	1.15	----	0.14	0.03	----	0.20	0.25	0.16	0.54	0.16	0.34	0.27	1.75	0.98	0.87	3.67	0.04	0.36	0.01	----	----
C_3H_8	8.35	2.76	0.10	0.04	----	0.18	0.22	0.28	0.72	0.34	0.26	1.18	1.59	0.62	1.64	3.80	0.10	0.47	0.12	6.79	7.04
C_4^-	0.82	0.18	0.12	0.12	0.22	0.50	0.36	0.42	0.48	0.34	0.49	0.58	0.95	0.76	0.31	0.42	0.13	0.40	0.32	0.11	0.43
NC_4	2.50	0.36	0.12	0.16	0.40	0.65	0.52	0.52	0.48	0.45	0.48	0.39	1.40	0.63	1.01	1.53	0.31	0.62	0.69	1.66	2.59
IC_4	0.88	0.18	0.02	0.02	0.06	0.15	0.09	0.12	0.12	0.09	0.10	0.08	0.29	0.13	0.21	0.32	0.07	0.13	0.15	0.52	0.81
C_5^-	0.32	0.06	0.03	0.02	0.06	0.15	0.18	0.18	0.20	0.16	0.14	0.31	0.29	0.16	0.14	0.17	0.05	0.20	0.22	0.33	0.56
NC_5	0.68	0.06	0.06	0.03	0.12	0.35	0.32	0.32	0.28	0.25	0.25	0.22	0.37	0.18	0.23	0.27	0.10	0.38	0.42	0.89	1.28
IC_5	0.45	----	0.03	0.02	0.06	0.18	0.14	0.14	0.12	0.11	0.11	0.10	0.15	0.09	0.12	0.14	0.06	0.21	0.22	0.73	1.04
C_6H_6	0.02	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	0.04	0.05
C_6H_{12}	0.10	----	----	----	----	----	----	----	----	----	0.03	----	----	----	0.03	----	----	----	----	0.24	0.32
C_6H_{14}	0.08	----	----	----	----	----	----	----	----	----	0.04	----	----	----	0.04	----	----	----	----	0.27	0.25
IC_6	0.12	----	----	----	----	----	----	----	----	----	0.10	----	----	----	0.07	----	----	----	----	0.27	0.46
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.68	0.22	0.19	4.69	0.37	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO_2	0.00	0.00	0.60	0.72	0.40	1.02	0.56	1.18	1.10	0.83	1.41	1.02	3.06	2.69	3.80	4.54	0.21	1.86	0.53	0.00	0.00
Total Gas Weight, Gms. (Hydrocarbon + CO + CO_2)	31.75	3.72	1.40	1.23	1.38	4.08	3.59	4.18	6.42	4.01	4.58	9.38	13.56	7.37	13.42	27.78	1.44	5.87	3.42	16.2	22.2

TABLE 14

Catalyst Breakup Tests: It was noted in Runs 193-139 and -140 that, with the stirrer speed at 750 rpm, a substantial amount of catalyst breakup had occurred. This breakup is a function of operating in the stirred autoclave and is not typical of ebullated bed operation. The next three runs were devoted to determining what kind of stirrer speed would eliminate catalyst breakup. The results are tabulated as follows:

Catalyst Breakup Tests
(Ketjen Catalyst, 70°F, 0 psig)

Run	Time Hrs.	Stirrer Speed, rpm	Observations
193-141	0.25	500	Catalyst intact
193-142	2.00	500	Catalyst broken up
193-143	2.00	200	Catalyst intact

On the basis of these results, it was decided to make all future runs at 200 rpm.

Temperature Effect: In Run 193-140, a definite exotherm was observed in the temperature range of 500°F to 650°F. Runs 193-144 and -145 were made to determine if the carbon black would be released by just coming up to 660°F and 750°F. The first run was extensive in length, taking about six hours because an attempt was made to keep the internal and external autoclave temperatures within 25°F of each other. As indicated below, the release of carbon black was essentially complete. The term carbon as used in the table below refers to carbon black and ash. Another interesting result to observe is the amount of gas yield which comes from both the ground rubber and slurry oil (anthracene oil), as also indicated below.

Temperature Comparison
(Ketjen Catalyst; 1,000 psig; 200 rpm,
Shut down on reaching temperature)

Run	Time Hrs.	Temp. °F	Gas Yield Grams	Carbon, Prod. / Carbon, Feed	Pseudo-DBP Number
193-144	6.0	660	3.7	0.97	--
193-145	1.5	750	1.4	0.89	72

The higher gas yield at the lower temperature undoubtedly results from the extraordinary length of Run 193-144.

Runs 193-147 and -148 were made at 460°F and 750°F, respectively, and held at that temperature for one hour. These results, and a comparison with Run 193-140 at 850°F, are given below. The low reaction temperature in Run 193-147 resulted in a thick tar-like product from which the carbon black was not released. The carbon black was "sprung" from the rubber in Runs 193-140 and -148. The amount of gas produced in Run 193-140 at 850°F was quite large because of the high reaction temperature.

Temperature Comparison
(Ketjen Catalyst; Held 1 Hr. at temperature; 1,000 psig)

Run	Temp. °F	Stirrer Speed rpm	Gas Yield Grams	Carbon, Prod. / Carbon, Feed	Pseudo-DBP Number
193-140	850	750	31.8	0.84	--
193-148	750	200	4.1	0.95	77
193-147	460	200	1.4	----	--

Two runs (193-160 and -161) were made to investigate the effects of 800°F and 850°F reaction temperatures on gas and solid yields and carbon quality. These runs are compared with Run 193-150 made at 750°F.

Temperature Comparison
(1/32" HDS-1441 Catalyst; 1,000 psig; 200 rpm)

Run	Temp. °F	Carbon Prod. / Carbon Feed	Hydrocarbon Gas Grams	Ratio: Gms Hydrocarbon Gas / Gms Rubber Charge	Pseudo-DBP Number
193-150	750	0.82	3.0	0.045	74
193-160	800	1.2	9.62	0.072	72
193-161	850	1 1	23.2	0.174	77

Runs 193-160 and -161 were made with double rubber and oil charges. Cracking was more severe at the higher temperatures as indicated by higher gas yields. Indicated carbon black products for Runs

193-160 and -161 were higher than carbon black in the feed. This is probably due to some entrained oil left in the carbon black during the product separation procedure.

Pseudo-DBP numbers were similar for the temperature range studied. The development of this test procedure is described in the Appendix.

Pressure Effect: Run 193-146 was made to determine if the desired results could be obtained at 500 psig as well as 1,000 psig. The data presented below indicate that the yield of carbon and ash is also quantitative and the gas yield is low. The level of carbon on the catalyst, which can be indicative of coke formation due to degradation of the oil in the system, was not significantly different and does not in either case indicate serious deactivation.

Pressure Comparison
(200 rpm, Ketjen CoMo Catalyst, Shut down on reaching 750°F)

Run	Time Hrs	Pres. psig	Gas Yield Grams	% Coke on Catalyst	Carbon, Prod. / Carbon, Feed
193-146	1.0	500	1.2	9.0	0.98
193-145	1.5	1000	1.4	13.0	0.89

Pseudo-DBP numbers were slightly higher for low pressure operations; 81 for Run 193-146 and 72 for Run 193-145.

Run 193-165 investigated the effect of 2,000 psig hydrogen pressure on product yields. The following table compares these data with Run 193-150 carried out at 1,000 psig.

Pressure Comparison
(1/32" HDS-1441, Held at 750°F for 1 hour, 200 rpm)

Run	Pressure	Carbon, Prod. / Carbon, Feed	Gas Yield Grams	DBP Number
193-165	2000	0.96	3.4	69
193-150	1000	0.82	4.2	74

The higher pressure produced slightly lower gas yield and pseudo DBP number.

Catalyst Comparison: A comparison of commercially available hydrotreating catalysts was made by comparing the results from Runs 193-148, -149, -150, -151, and -163 (Table 15). Four of the catalysts were cobalt molybdate on alumina, which have different pore size distributions, and the fifth was a nickel molybdate on alumina. The gas yields, with the exception of the high values with HDS-1442B (previously known as HDS-2B) were essentially identical.

The effect of the absence of catalyst on carbon yield and quality was investigated in Run 193-156. A comparison of this run with Run 193-148 follows:

Temperature - 750°F, Hydrogen Pressure - 1,000 psig, 200 rpm

Run	Catalyst	Carbon, Prod. / Carbon, Feed	Gas Grams
193-148	1/32" Ketjen (2280)	0.95	4.1
193-156	None	1.00	4.6

Run 193-157 was carried out using a nitrogen (1,000 psig) rather than hydrogen atmosphere and no catalyst. A comparison with Run 193-156 is presented below.

Run	Catalyst	Pressure (1000 psig)	Carbon, Prod. / Carbon, Feed	Gas Grams	Pseudo-DBP Number
193-156	None	Hydrogen	1.00	4.6	69
193-157	None	Nitrogen	1.04	9.4	77

Pseudo-DBP numbers were similar for both runs. There was little or no coke laydown in the reactor in any of these studies, even with nitrogen and no catalyst.

AUTOCLAVE CATALYST COMPARISON

(1,000 psig; 1 Hr at 750°F; 200 rpm)

Run	Catalyst	Catalyst Feed, Gms.	Carbon Black + Ash in Feed (Gms.)	Catalyst Product, Gms.	Carbon Black + Ash In Product, Gms.	Total Gas Yield Gms.	Ratio: Gms Total Gas / Gms Rubber
193-148	Ketjen CoMo (HRI 2280)	10	23.8	12.3	22.6	4.1	0.061
193-149	HDS-3B NiMo (HRI 2604)	10	23.8	11.3	22.0	3.6	0.054
193-150	HDS-1441 CoMo (HRI 2959)	10	23.8	14.7	19.4	4.2	0.063
193-151	HDS-1442B CoMo (HRI 3071)	10	23.8	13.0	23.1	6.4	0.096
193-163	Nalco 471 CoMo (HRI 2308)	20	47.6	23.8	46.9	5.9	0.044

TABLE 15

The most significant difference in yields was in the amount of gas produced in the nitrogen atmosphere. The gas make in Run 193-157 was quite high (9.4 grams) as compared to either Runs 193-148 or 193-156. A check of the gas composition showed 5.7 grams of carbon monoxide and carbon dioxide, or one-half of the gas produced. Based on the amount of oxygen in the feed available for conversion to carbon monoxide, only 3.3 grams of carbon monoxide could be formed, assuming all the oxygen in the feed was converted to carbon monoxide. The material balance was also high (102%).

Oxygen in the feed rubber was calculated by difference. Because of possible inaccuracies in any number calculated by difference, the percent of oxygen was later determined by the Unterzaucher Method, which has an accuracy of $\pm$ 0.3 weight percent. The Unterzaucher Method gave 4.59 weight percent versus 2.7 weight percent by difference. The higher oxygen concentration by the Unterzaucher Method could account for the high carbon monoxide and carbon dioxide yields.

Slurry Oil Effect and Comparisons: Run 193-152 was made to determine if substituting tetralin (tetrahydronaphthalene) as the slurry oil in place of anthracene oil would have any effect. Little difference was noted in the gas yields, which probably indicates that the majority of the gas produced came from the rubber. In addition, the amount of carbon black plus ash was about the same. The runs were conducted at 1,000 psig; 750°F for one hour; 200 rpm; and with Ketjen catalyst. The comparison data is as follows:

Run	Slurry Oil	Gas Yield Grams	Carbon, Prod. / Carbon, Feed
193-148	Anthracene Oil	4.1	0.95
193-152	Tetralin	4.0	0.97

The amount of hydrocarbon gases (C_1-C_6) is given in Table 14.

Run 193-158 was made without anthracene oil dilution in an effort to produce carrier oil similar to that which would be recycled in

continuous operation. Only raw rubber and catalyst (Ketjen, HRI 2280), was charged to the autoclave, which was operated at 750°F and 1,000 psig. The product was visually similar to the initial rubber charge, but was tar-like to the touch. However, no free liquid was produced. The gas yield was 13.6 grams based on a 200-gram charge of rubber. Based on the normal rubber charge of 67 grams, the gas yield would be corrected to approximately 4.6 grams, which is similar to a run with anthracene oil (Run 193-148, 4.1 grams, gas). This indicated again that the gas yield was formed from rubber cracking. More significantly, these results indicated that the release of the carbon from the rubber proceeded through reaction of rubber with oil.

Run 193-159 was similar to Run 193-148 except that a double charge of anthracene oil, rubber, and catalyst was used. The gas yield results were nearly double the gas yield of Run 193-148, as was expected.

Run	Gas Yield, Grams	Pseudo-DBP Number
193-148	4.1	77
193-159	7.4	73

Run 193-162 was made with just anthracene oil and catalyst (no rubber) to determine the contribution of anthracene oil to gas and liquid product yields. A comparison of the ASTM distillation for anthracene feed and product oil from Run 193-162 is as follows:

	Anthracene Feed	Oil Product
Gravity, °API	-7.3	-5.7
IBP	496	448
30%	632	598
Gas Yield, Grams	---	1.4

These data indicate that some hydrogenation, but little cracking, took place. A comparison with a similar run using rubber feed follows.

Run	Feed	Gas Yield, Grams
193-150	Rubber + Anthracene	4.2
193-162	Anthracene	1.4

Both runs were made using HDS-1441 catalyst at 750°F and 1,000 psig hydrogen pressure. The ASTM distillations for these runs are presented in Table 16. A much higher gas yield is evident in Run 193-150 indicating that a major proportion of the gas product came from the rubber at 750°F.

To determine the reactivity of the 2 to 4 percent fibers contained in the rubber feed, Run 193-164 was made on the fibers sent to HRI by Uniroyal Chemical. The run was aborted because of a plugged vent line, and no data were collected.

Runs 193-166-1 and -2 were parts of a two-stage run. The first stage, 166-1, was a thermal cracking operation with no catalyst and just rubber and anthracene oil feed. After reacting for one hour at 750°F and collecting the product gas, the reactor was cooled and opened. Ten grams of 1/32" HDS-1441 catalyst was added to the liquid product and the reactor was closed. The second stage, 166-2, was then run at 750°F for one hour.

Data exists on the first stage from a previous run made at the same conditions (193-156). Analytical results from the two-stage run (193-166) indicated no upgrading of the carbon black product in the second catalytic stage after thermal cracking in the first stage. Pseudo-DBP numbers were the same for the carbon black from both stages (67 to 69).

Sulfur Determination: Sulfur analyses were obtained on the carbon black from Runs 193-145, -148, -156, and -157. The data are presented in Table 17. A sulfur material balance was done on autoclave Run 193-148. The results are as follows:

TABLE 16

AUTOCLAVE PRODUCT OIL ASTM DISTILLATION

Run	193- 162	150
Date	10-15-71	8-27-71
Gravity, °API	-5.7	-2.5
Distillation, °F		
IBP	448	228
10%	524	515
20%	568	582
30%	598	622
40%	622	
50%	650	
60%		
70%		
80%		
90%		
EP		
REC		39
RES		60
Loss		1
V % at 400°F	-	3
V % at 600°F/650°F	31/50	25/37

AUTOCLAVE PRODUCT SULFUR DISTRIBUTION

Run	Temperature, °F	Pressure (1000 psig)	Catalyst	Charge		Products			
				Sulfur in Rubber, Gms	Sulfur in Oil, Gms	Sulfur in Carbon Black, Gms	Sulfur in Oil, Gms	Sulfur in Gas, Gms	Sulfur on Catalyst, Gms
193-145	Shut down on reaching 750°F	Hydrogen	1/32" Ketjen	0.96	1.15	0.65	----	----	----
193-148	Held at 750°F for 1 hour	Hydrogen	1/32" Ketjen	0.96	1.15	0.78	0.80	0.06	0.26
193-156	Held at 750°F for 1 hour	Hydrogen	None	0.96	1.15	0.79	----	----	----
193-157	Held at 750°F for 1 hour	Nitrogen	None	0.96	1.15	0.88	----	----	----

NOTE: The dashed horizontal line indicates that no data was obtained.

TABLE 17

	Sulfur, Grams
Feed	
Rubber	0.965
Anthracene Oil	1.152
Total	2.117
Products	
Gases - Vent	0.054
- Flash	0.006
Oil	0.805
Carbon Black and Ash	0.775
Catalyst	0.255
Total (92% Material Balance)	1.895
(100% Material Balance)	2.060
Sulfur, Prod./Sulfur, Feed	0.973

The quantity of sulfur in the carbon black and ash (0.775 grams) indicates that most of the sulfur in the rubber was retained in the carbon black plus ash product.

One-Quarter-Inch Rubber Feedstock Experiments: Two runs were made in the stirred autoclave reactor to determine if the carbon black could be "sprung" from one-quarter-inch ground whole tires at 850°F. All previous runs were made using the more expensive -24 mesh ground tires with all but two to four percent of the fibers removed. The fibers were not removed by Uniroyal from the larger one-quarter-inch rubber, making this stock less expensive due to decreased capital and operating expenditures for grinding and fiber separation.

Run 193-167 was made using the rubber as received from Uniroyal. The 134-gram rubber charge was diluted with 366 grams of hydrogenated anthracene oil. The rubber charge consisted of approximately six to eight percent fibers.

After reacting the charge at 850°F for one hour at 1,000 psig pressure, the product was dumped from the reactor and separated into liquid and solid fractions.

The 100+ mesh solids were screened out and benzene extracted. Among these solids was found 0.11 grams of unreacted rubber (0.09% of rubber feed). This rubber was probably insulated by the large unreacted fiber strands and was not exposed to the 850°F reaction temperature. The remaining 100+ mesh solids consisted of 0.6144 grams of material of which 86.0 percent were glass fibers and a small amount of fine ash. The remaining 14 percent combustible material was probably entrained carbon black. It should be noted that only 7 weight percent of the fibers in the feed remained unreacted.

The pseudo-DBP number for the carbon black was higher than all previous autoclave runs. This was probably due to the absence of fine fibers in the carbon black. With the -24 mesh rubber feed, most of the glass fibers remain in the carbon black. With the one-quarter-inch stock, the fibers were larger and were easily separated from the carbon black with a 100 mesh screen.

A second run (193-168) was made in the autoclave reactor to determine if there were any "hard to react" rubber species in the one-quarter-inch rubber feed. All visible pieces of fibers were removed from the rubber charge stock and only the rubber was charged to the reactor (134 grams). The rubber was diluted with 266 grams of hydrogenated anthracene oil and reacted at 850°F for one hour at 1,000 psig pressure.

The products were separated as in Run 193-167. The +100 mesh solids consisted of only 15.7 weight percent ash indicating only a small percentage of glass fibers. The remaining 84.3 weight percent combustible material was probably unreacted rubber and some entrained carbon black. The combustible material amounted to only 0.4 weight percent on rubber feed.

As in Run 193-167, the pseudo-DBP number obtained in Run 193-168 was higher using one-quarter-inch stock than using -24 mesh fine ground tires. Again, the absence of the glass fibers in the carbon black product probably boosts the DBP absorption number.

Discussion of Results

The major emphasis of the experimentation was centered around determining at what conditions the carbon could be "sprung" from the rubber in essentially a quantitative yield. Temperatures in the range of 460°F to 850°F; pressures of 500, 1,000, and 2,000 psig; residence times of from less than one hour to six hours; and a total of five catalysts were investigated. The test results demonstrate that the carbon black can be separated from the rubber and the rubber converted into an oil over a wide variety of operating conditions.

The primary structure of the black, as determined by pseudo-DBP number, was essentially constant and independent of any variables studied. A tabulation of the pseudo-DBP results is presented in Table 18.

One of the more interesting results was the apparent superiority of black obtained from one-quarter-inch ground tires over that from -24 mesh ground tires. It is more likely that the test is affected by the presence of ground glass fibers. With the smaller charge stock, the glass fibers are ground to a size which makes them very difficult to identify and separate from the carbon black product. However, the unreacted glass fibers are easily separated from the product when the feed is one-quarter-inch ground tires.

In general, the temperature at which the reaction was carried out seemed to have little effect on the quality of the carbon. At all temperatures above 660°F, the carbon was "sprung" from the rubber. However, at a temperature of 460°F, no separation was obtained. At this temperature, a solid gel was removed from the stirred autoclave. Benzene extraction of the gel yielded no free carbon or ash. Therefore, there is some threshhold temperature between 460°F and 660°F at which reaction begins which is sufficient to "spring" the carbon black.

The major effect of increasing reaction temperature is to increase the amount of gas produced. Figure 2 shows this effect. A blank run made with slurry oil, but without rubber, indicates that about one-third of the gas make at 750°F comes from the slurry oil. This proportion is unlikely to be constant as

PSEUDO-DBP NUMBERS AT VARIOUS OPERATING CONDITIONS

Run	Time at Reaction Temp Hrs	Temp, °F	Hydrogen Pressure, psig	Catalyst	Pseudo-DBP Number
193-145	0	750	1000	1/32" Ketjen CoMo on Alumina	72
193-146	0	750	500	1/32" Ketjen CoMo on Alumina	81
193-148	1	750	1000	1/32" Ketjen CoMo on Alumina	77
193-149	1	750	1000	1/32" NiMo on Alumina	68,73
193-150	1	750	1000	1/32" HDS-1441 CoMo on Alumina	74
193-151	1	750	1000	1/32" HDS-1442B CoMo on Alumina	69
193-156	1	750	1000	None	69
193-157	1	750	1000 (N_2)	None	77
193-158	1	750	1000	1/32" Ketjen CoMo on Alumina	69
193-159	1	750	1000	1/32" Ketjen CoMo on Alumina	73
193-160	1	800	1000	1/32" HDS-1441 CoMo on Alumina	72
193-161	1	850	1000	1/32" HDS-1441 CoMo on Alumina	77
193-163	1	750	1000	1/16" Nalco CoMo on Alumina	70
193-165	1	750	2000	1/32" HDS-1441 CoMo on Alumina	69
193-166	1;1*	750;750	2000;2000	None; 1/32" HDS-1441 CoMo on Alumina	67,69
193-167	1**	850	1000	None	90
193-168	1**	850	1000	None	82

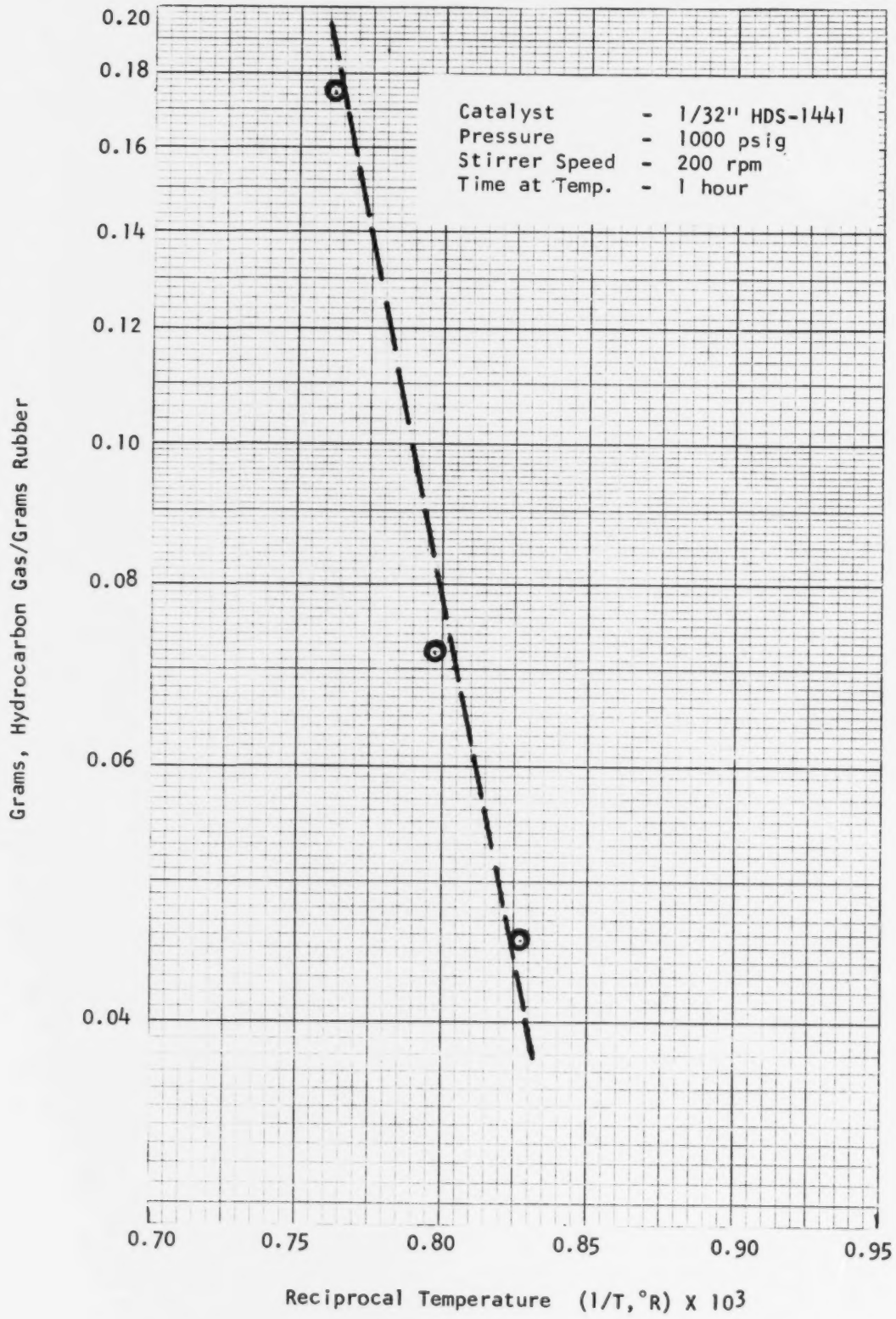
* This experiment was a simulation of a two-stage operation. The catalyst was added after the first part of the experiment was completed without catalyst.

** $\frac{1}{4}$" rubber, all other rubber was -24 mesh.

TABLE 18

FIGURE 2

STIRRED AUTOCLAVE TESTS - EFFECT OF TEMPERATURE ON HYDROCARBON GAS MAKE



temperature varies.

No significant differences in carbon quality were observed in the autoclave tests as a result of varying the total pressure among 500; 1,000; and 2,000 psig.

One of the more interesting results was the effect of the nitrogen atmosphere used in Run 193-157 in place of the normal hydrogen atmosphere. A large proportion of the oyxgen in the rubber was converted to CO and CO_2. Normally, this reaction is suppressed by the presence of hydrogen and catalyst which converts the oxygen to water. Additional work in this area was not carried out since coke formation in liquid and solid hydrocarbon continuous flow systems is normally extensive at temperatures exceeding 750°F in the absence of hydrogen.

Catalyst seems to have had little effect on carbon quality since the carbon had the same properties independent of the type of catalyst used or the presence or absence of catalyst. No improvement was noted in carbon quality after completing a run without catalyst (Run 193-166) and then repeating the run with catalyst added to the reactor and without removal of the products from the reactor.

Unfortunately, in this series of tests, the amount of slurry oil used is large in comparison with the oil obtained from hydrogenating the rubber. Therefore, no meaningful information can be obtained from analysis of the liquid products from this sequence of experiments.

The lack of reaction of the rubber when slurry oil was not charged to the stirred autoclave (Run 193-158) indicated that the freeing of the carbon from the rubber proceeds through solvent attack on the rubber. If it were only a matter of heating the rubber in a hydrogen atmosphere, then liquefaction should have proceeded directly in the reactor. It appears that the rubber was softened, but no liquid was formed.

CATALYTIC PILOT PLANT OPERATIONS

General

A total of 11 continuous catalytic pilot plant runs were made. Eight of these were made in a single-stage unit. A summary of the operating conditions used for these runs is given in Table 19. Three two-stage runs were made with the first stage non-catalytic and the second stage catalytic. The operating conditions used for these runs is summarized in Table 20.

Unit Description

Single-Stage Operation: A simplified flow sheet of the single-stage H-Rubber pilot plant used for catalytic operations is presented in Figure 3.

The pilot plant consisted of a rubber-slurry oil charge pot piped to a positive displacement piston pump for metering the rubber-oil slurry to the unit. Slurry pumping tests, described in the Appendix, were carried out to determine the optimum concentration of ground rubber in oil.

With the exception of Run 144-143, where the slurry was injected at the reactor inlet, the rubber-oil slurry was pumped to the top of the preheater where it was mixed with the preheated hydrogen feed and the internal recycle oil stream from the reactor. The mixture flowed down through the preheater and into the bottom of the reactor.

Unit 144 reactor has a 0.614-inch inside diameter with a reaction volume of 400 cc. Unit 177, which is functionally identical to Unit 144 and was used for two of the runs in the series, has a reactor with a 0.815-inch inside diameter and a reaction volume of 1,000 cc. Screens were used at the bottom and top of these

OPERATING PROGRAM

SINGLE-STAGE CATALYTIC H-RUBBER RUNS

Run	144-143	144-144	144-145	144-146	144-148	177-72	177-73	144-156
Reactor Temperature, °F	750	800	800	800	850	850	850	850
Hydrogen Pressure, psig	1000	1000	1000	1000	1000	2250	2250	1000
Catalyst	1/32" HDS-1441	1/16" Nalcomo 471		-----	1/32" HDS-1441	1/16" Nalcomo 471		-----
HRI Number, Catalyst	2959	2308	----------		2959	2308	----------	
Total Feed Rate, Diluent Oil + Rubber, Gms/Hr	800	800	900	900	900	900	950	800-1100
Rubber Concentration, W %	10.0	12.5	11.0	11.0	11.0	12.8	5.3	6.0-11.0
HRI Number, Rubber	3219	3219	3219	3219	3219	3221	3221	3286
Rubber Size, Mesh	-24	-24	-36	-36	-36	-36	-50	-24
Use of Filtered Liquid Product as Diluent Oil	No	Yes	Yes	Yes	Yes	No	No	Yes
Internal Recycle Rate, cc/Hr	12,000	12,000	20,000	20,000	30,000	81,000	81,000	20,000
Length of Run, Hrs	2	8	26	23	14	3	6	123

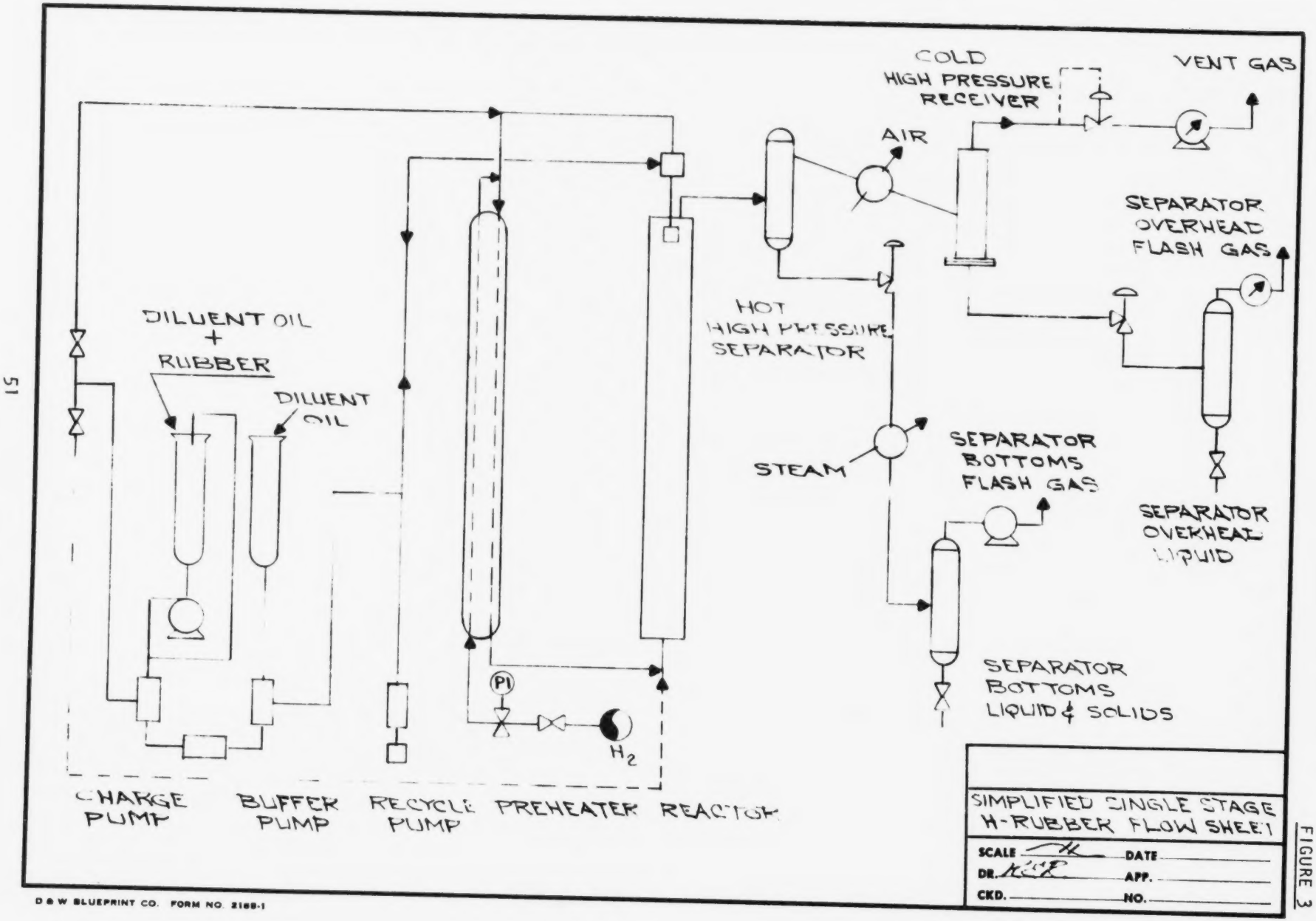
TABLE 19

OPERATING PROGRAM

TWO-STAGE H-RUBBER RUNS

Run 144-	151	152	153
1st Stage Non-Catalytic Reactor Temperature, °F	850	850	800
2nd Stage Catalytic Reactor Temperature, °F	800	785	790
Hydrogen Pressure, psig	1000	1000	1000
Catalyst	1/32" HDS-1441		
HRI Number, Catalyst	3161		
Total Feed Rate, Diluent Oil + Rubber, Gms/Hr	650; 1,400	1118	992
Rubber Concentration, W %	8;14	12.1	8.0
Rubber Size, Mesh	-36	-36	-36 (Elutriated to remove fibers)
Use of Filtered Liquid Product as Diluent Oil	Yes	Yes	Yes
Internal Recycle Rate, cc/Hr - 1st Stage	45,000	45,000	45,000
2nd Stage	12,000	19,000	19,000
Length of Run, Hours	7	4	7

TABLE 20



SIMPLIFIED SINGLE STAGE
H-RUBBER FLOW SHEET

SCALE ____ DATE ____
DR. ____ APP. ____
CKD. ____ NO. ____

D & W BLUEPRINT CO. FORM NO. 2168-1

FIGURE 3

reactors to prevent catalyst from leaving the reactor. This technique is limited to small ebullated bed pilot plant reactors of this type and is not used in larger equipment.

At the top of the reactor, the major portion of the reaction liquid was drawn from the top of the catalytic zone through an outlet pipe into a set of check valves. The reactor liquid recycle, which is referred to as the internal recycle, then joined the fresh feed before entering the preheater. A buffer oil pump was used to inject slurry oil containing no rubber into the line between the internal recycle pump and the check valves to prevent solids from migrating to the pump piston. The remainder of the reactor effluent, consisting of the gaseous products and the net liquid, was sent to a hot high pressure separator. In order to prevent naphtha from condensing, this separator was maintained at approximately 500°F. If the naphtha went with the heavy liquid and solids to the filtration step, it would be lost by vaporization.

The overhead gas product from the separator went through a transfer line, in which a significant amount of condensation occurred because of a heat leak, and into an ambient temperature, high pressure receiver. In this receiver, the product was again separated into a vapor and a liquid. Vent gas from the top of the receiver was let down to atmospheric pressure and its volume was measured by a wet test meter.

Condensed liquid (separator overhead product) was then continuously let down to atmospheric pressure and collected in a low pressure receiver. The flash gas from this liquid was measured by a wet test meter.

The liquid-solid product from the hot separator was continuously reduced to atmospheric pressure through a control valve and cooled by contact through the transfer pipe wall with a steam tracing. Flash gas and slurry were then separated in an atmospheric receiver and the gas was measured and sampled.

The separator bottoms liquid product was pressure filtered in a 12-inch diameter, single plate filter. Because of the inefficient filtering method used, the filter cake generally contained

up to 50 weight percent of physically entrained gas oil. For laboratory analyses to determine the amount of carbon black in the cake, a sample of the cake was benzene extracted to remove the entrained oil, and dried.

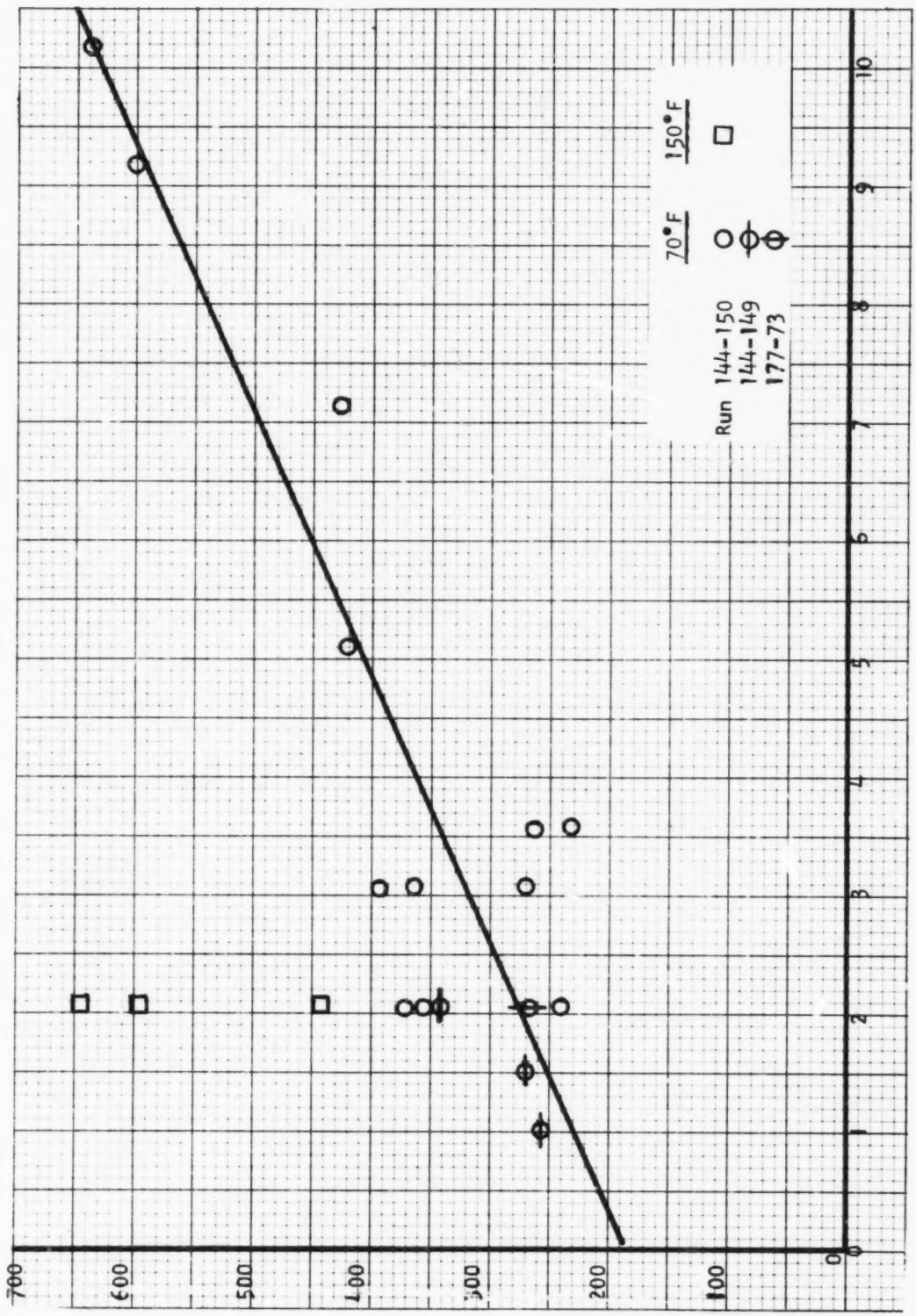
The filtering procedure consisted of charging up to 4,000 grams of the separator bottoms liquid product to the inlet of the filter (filter capacity was approximately 4,000 cc). The charged liquid layed on top of three 12-inch diameter filter papers inside the flanged vessel. Three filter papers were used to add strength to avoid breakthrough at elevated pressures. Nitrogen pressure (150 psig) was applied on top of the liquid to pressure it through the filter cake and filter paper pores. The liquid was collected in a vessel at the filter outlet. If more than 4,000 grams was to be filtered, the remaining slurry was poured into the filter on top of the already filtered cake and the filter was pressured up again with nitrogen.

The filtration was finished when the nitrogen blew through the filter cake and out the filter product line. When the filtration operation was completed, the filter flange was opened and the cake and filter papers were lifted off the supporting screen. The cake, filter paper, and pressure filtered liquid product were weighed to obtain product yields. In most runs, the pressure filtered liquid product was recycled as slurry oil.

Filtration rates were a function of temperature and cake thickness. Therefore, the filtration was performed at temperatures ranging from 70°F to 300°F depending on the estimated quantity of solids in the liquid charge. Figure 4 shows a graph of weight of filter cake versus filtration time. The data points are typical and and were taken from the filtrations done during Runs 144-149 and -150 and 177-73. The plot shows that the filtration time is linearly dependent on the quantity of cake present and is considerably affected by temperature. For cakes normally taking 9 to 10 hours to filter at room temperature, raising the temperature from 70°F to 150°F cut the filtration time by 80 percent.

FIGURE 4

H-RUBBER PRESSURE FILTRATION OPERATION



Two-Stage Operation: A flow sheet of the H-Rubber pilot plant for this operation is presented in Figure 5. The unit used for the single-stage operation was modified by coupling it to a second reactor having an independent product handling system.

Total product effluent from the first reactor went to the top of the second stage preheater, down through the preheater, and up into a second 0.614-inch inside diameter reactor.

As in the first stage, the major portion of the reactor outlet fluid was recycled back to the inlet and a product stream was taken off at the top reactor flange.

The product leaving the second stage reactor was handled in an identical manner to that described earlier for the single-stage operation.

Operating Procedure

For the initial catalyst run (144-143) using an ebullated bed, the rubber was slurried with regular anthracene oil in the charge pot and injected directly into the hot external recycle stream at the reactor inlet. In an effort to eliminate the plugging of the reactor that occurred in this run, the injection point of the rubber slurry was changed from the reactor inlet to the preheater inlet for the remaining ebullated bed runs. The objective of this change was to break down the physical size and consistency of the rubber and cause good dissolution in the slurry oil. It was thought that the normal ebullated bed technique of injecting the feed into the hot internal recycle stream at the reactor inlet was not adequate to accomplish this end. Other changes after Run 144-143 were the use of hydrogenated anthracene (in place of regular anthracene) for startup and the use of recycle (pressure filtered) liquid as slurry oil as soon as product was made.

The operating procedure for all ebullated, catalytic runs except Run 144-143, as mentioned above, is described as follows.

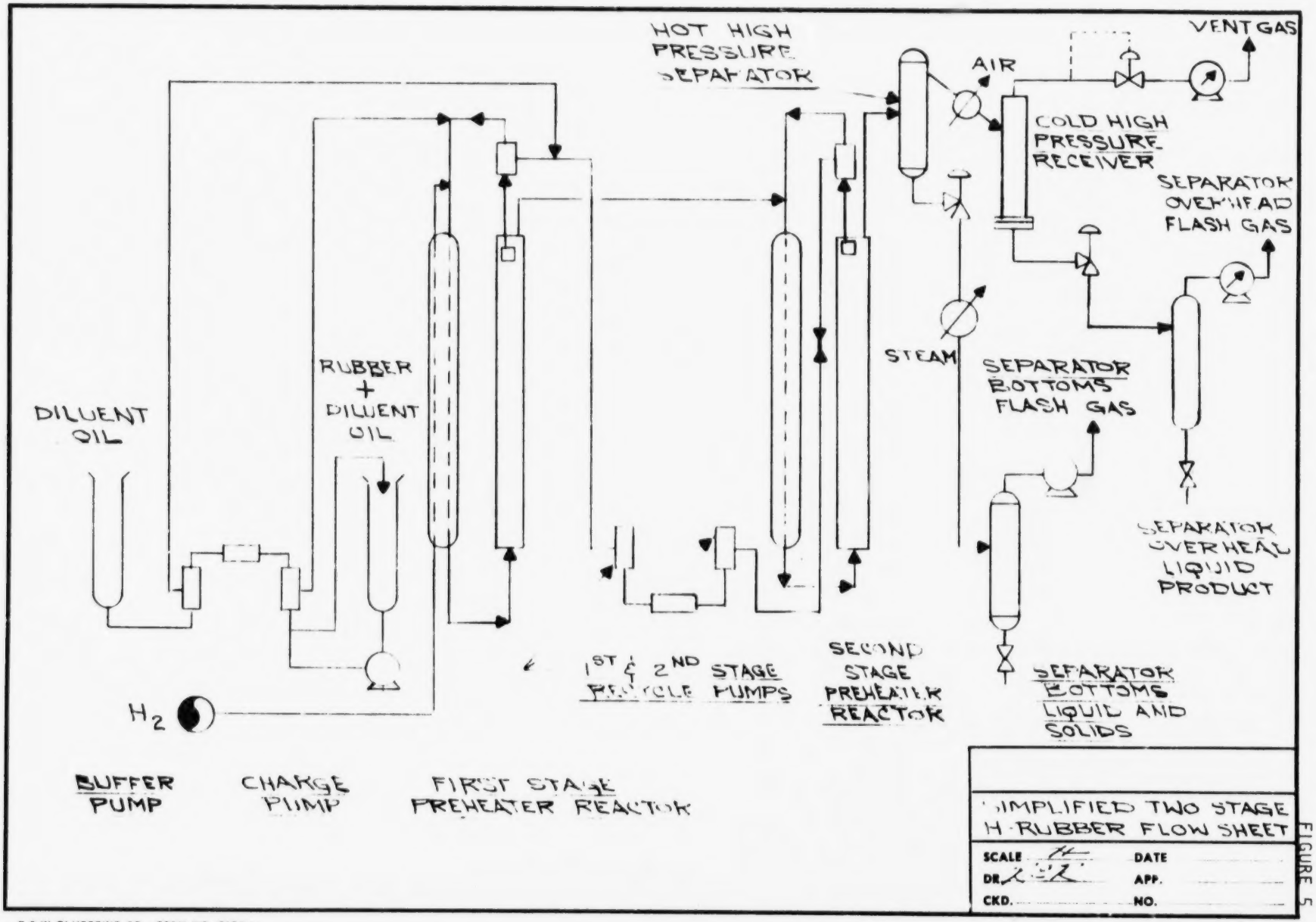


FIGURE 5

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The unit pressure and hydrogen vent gas rate were established prior to charging the oil feed. The reactor and lead bath preheaters were turned on and the reactor was heated to 300°F. The preheater temperatures were usually kept at or between 10 to 20°F lower than the reactor lead bath temperatures. Earlier experimental work in these units has shown that the lead bath and internal reactor temperatures are identical.

When the reactor temperature reached 300°F, pumping of anthracene oil into the unit was initiated at the desired rate. The reactor temperatures were brought up to approximately 700°F. Internal recycle flow was then slowly started. As the reactor temperature was brought up to the run temperature, the internal recycle rate was slowly raised to the desired value.

When the unit was lined out at the desired temperature and flow rate, rubber and slurry oil were both added at a fixed rate to the stirred charge pot. Over a period of a few hours, the rubber concentration in the charge pot was increased to the desired concentration. The products coming from the unit were recovered and identified as separator bottoms liquid (containing carbon black), separator overhead liquid, vent gas, separator bottoms flash gas, and separator overhead flash gas. The separator bottoms liquid was pressure filtered to remove the solids. The resultant pressure filtered liquid was recycled as slurry oil in place of anthracene oil. Anthracene oil was used as makeup oil when needed.

No significantly different procedures were used for two-stage operations.

Results

Single-Stage Operations - Run 144-143: After lining out the unit on regular anthracene oil (HRI 3116), the feed was brought to a 10 weight percent rubber concentration over a one-hour period. After reaching the 10 percent concentration, a rate of 80 grams per hour of rubber was fed to the reactor for one

hour. At this time, the reactor pressure drop built to 20-25 psig and then sudden'y jumped to 75 psig.

Rubber feed was cut out and only regular anthracene oil was fed to the unit. The plug could not be cleared and the unit was shut down.

The reactor was opened and the catalyst dumped. Some large agglomerates ($\frac{1}{2}$-inch) were found in the free-flowing catalyst. Glass fibers were observed through a microscope in the ash from these agglomerates. Fibers received from Uniroyal were also ashed and found to contain glass fibers.

Fibers in the rubber feed were reported by Uniroyal to range from two to four weight percent.

Quite a bit of tar-catalyst agglomerated material was found on the walls at the reactor inlet. The tarry substance had a thick consistency, but there was little, if any, coke. No products were collected for analyses because of the briefness of the run.

Single-Stage Operations - Run 144-144: In order to prevent plugging of the reactor, the catalyst was changed from 1/32-inch diameter to 1/16-inch diameter, the temperature was raised from 750°F to 800°F, and the feed inlet point was moved to the pre-heater inlet instead of the reactor inlet.

When the unit was lined out, 100 grams per hour of rubber was fed to the charge pot, which contained anthracene oil. When rubber feed was initiated, separator bottoms were filtered and returned to the charge pot as recycle. Hydrogenated anthracene oil was used as recycle makeup when needed.

The run lasted eight hours (0900-1700, 10/2/71) before it was shut down with a differential pressure of 150 psig across the reactor. The reactor pressure drop had started to build after three hours on stream.

The reactor was opened and some fibers and what looked like raw rubber was found on the inlet bubble cap. The catalyst was pushed up against the top screen, which is 6.5 feet above the reactor inlet. The catalyst did not dump freely, but was not coked up. The check valves at the top of the reactor were clean, as were the reactor inlet lines.

The dumped catalyst was benzene extracted. Large, black chunks of elastic material were found mixed with the catalyst after the extraction. This was assumed to be rubber. A sample of this rubber-catalyst mixture was ashed to see if the fibers had concentrated with these pieces of rubber. Microscopic examination showed hardly any glass fibers. It may be that, during the shutdown, unreacted rubber particles from other parts of the system were washed into the reactor. Because of catalyst fines mixed with the ash, quantitative analysis was not attempted.

The sample of rubber (HRI 3219) used for this run visually seemed to contain many more fibers than the original rubber sample (HRI 3184) used for the stirred autoclave experiments. Discussions with Uniroyal indicated that the fiber content was variable and a function of their operating variability from day to day. There was some suspicion that glass fibers, which tended to ball up near the inlet, contributed to the operating difficulties. Fiber separation experiments were carried out in an attempt to improve unit operability. These tests are described in the Appendix.

In this run, carbon black product was filtered out of the separator bottoms liquid. Pseudo-DBP analysis of the benzene extracted carbon black was 73/75. No other analyses were performed.

Single-Stage Operations - Run 144-145: The internal recycle rate was increased to 20,000 cc per hour during this run in an effort to provide better fluidization in terms of reducing catalyst slugging in the reactor. After three hours on rubber feed, the reactor differential pressure began to build.

Sixteen hours after startup, the rubber feed was switched to -36 mesh rubber, made by screening the -24 mesh rubber received from Uniroyal, in an effort to determine if coarse particles were the cause of the plugging. The change to the -36 mesh rubber did not help and the unit was shut down with a differential pressure across the unit of 1,500 psig after 26 hours on

rubber feed.

The reactor was opened and the catalyst bed was found up against the top screen of the reactor. The top screen, bubble cap, and piping between the preheater and reactor were clean. The catalyst was drilled out with a wire and dumped. Soft, gummy material was found with the catalyst.

ASTM distillations of the pressure filtered liquid and separator overhead are listed in Table 21, along with data for Runs 144-146 and 144-148. The boiling range of the pressure filtered liquid (0.5°API) was 416°F (Initial Boiling Point) to 640°F at 50 volume percent distilled. The ASTM distillation boiling range of the separator overhead (30.6°API) was 160°F (IBP) to 532°F end point. It should be noted that the oil products are not pure products of the rubber hydrcgenation reaction, but contain hydrogenated anthracene oil used as startup oil.

Sulfur analyses on the liquid products show that the pressure filtered liquid (gas oil) was desulfurized to 0.07 weight percent sulfur in the ebullated bed. The separator overhead (naphtha) was only partially desulfurized (0.53 weight percent sulfur) due to its being completely vaporized in the reactor and, therefore, having a comparatively low residence time.

Pseudo-DBP analyses ranged from 67 to 69, equivalent in structure to Run 144-144 carbon black.

A summary of the individual product yields and total material balance (89.9%) is listed in Table 22.

Single-Stage Operations - Run 144-146: Run 144-146 was made at the same operating conditions as Run 144-145, but -36 mesh rubber (HRI 3219) was used from the beginning of the run.

Even with the smaller particle size rubber feed and partial removal of the fibers, the reactor started to plug within one hour of startup. The run was shut down with an overall unit differential pressure of 2,000 psig after 23 hours on rubber feed.

CATALYTIC EXPERIMENTS - LIQUID PRODUCT INSPECTIONS

Period	----- 144-145-2 ------		----- 144-146-1 ------		----- 144-148-1 ------	
Product	Separator Overhead	Pressure Filtered Liquid	Separator Overhead	Pressure Filtered Liquid	Separator Overhead	Pressure Filtered Liquid
Gravity, °API	30.6	0.5	34.7	1.3	24.6	0.9
ASTM Distillations, V %						
IBP, °F	160	416	164	400	168	398
10%	228	500	226	498	225	488
30%	296	580	294	558	308	570
50%	342	640	338	616	378	622
70%	384	---	380	---	464	---
90%	460	---	424	---	670	---
FBP	532	---	496	---	---	---
V % @ 600°F	---	37	---	45	---	42
V % @ 650°F	---	56	---	65	---	62
W % Sulfur	0.53	<0.07	0.88	<0.07	0.23	<0.07

TABLE 21

The reactor was opened and the catalyst bed was found against the top screen. Some gummy material was found on the top screen. The bubble cap was also covered with this material.

Sulfur analyses on the liquid products show that the pressure filtered liquid (gas oil) was desulfurized to 0.07 weight percent sulfur in the ebullated bed; but, the separator overhead (naphtha), as in Run 144-145, was only partially desulfurized (0.88 weight percent sulfur) due to low naphtha residence time in the reactor.

Pseudo-DBP analyses ranged from 66 to 72, equivalent in structure to Runs 144-144 and 144-145 carbon blacks.

The carbon black product from this run was evaluated in rubber compound. The results are included in the Product Evaluations section of this report. The Uniroyal DBP absorption number (67) checked with the HRI pseudo-DBP number (66 to 72). After evaluating the HRI produced carbon black, the conclusion was that "the low DBP absorption, low viscosity, low modulus, and high tensile strength" of the HRI catalytically produced black "are characteristic of low structure, highly reinforced blacks". Blacks of this type are of significant commercial value.

A summary of product yields and overall material balance (94.0%) are listed in Table 22.

Single-Stage Operations - Run 144-148: This run was made using the smaller 1/32-inch HDS-1441 (HRI 2959) catalyst. From a series of ebullation tests done in a lucite tube, it was indicated that ebullation could be improved by using the smaller catalyst and a higher internal recycle oil flow. The reactor temperature was raised to 850°F to increase the rubber cracking rate in an attempt to eliminate partially reacted rubber particles from the bed.

Differential pressure across the reactor began to build after two hours on rubber feed and the run was terminated 12 hours later.

TABLE 22

CATALYTIC PILOT PLANT RUNS

SUMMARY OF YIELDS AND OVERALL MATERIAL BALANCES

Period	144-145-2	144-146-1A/1B
W %		
CH_4	0.13	0.37
C_2H_4	----	----
C_2H_6	0.15	0.43
C_3H_6	----	----
C_3H_8	0.16	0.42
C_4H_8	0.13	0.34
C_4H_{10}	0.23	0.43
C_4 Iso	0.08	0.14
C_5H_{10}	0.08	0.18
C_5H_{12}	0.13	0.30
C_5 Iso	0.10	0.23
C_6H_{12}	0.01	0.01
C_6H_{14}	----	----
C_6 Iso	----	----
Naphtha	8.54	----
Gas Oil	61.89	77.20
Solids + Entrained Oil	18.29	13.98
TOTAL	89.9	94.0

The reactor was opened and the catalyst was dumped. A thick, tar-like substance, which had the appearance of partially converted rubber, was mixed with the catalyst.

ASTM distillations of the pressure filtered liquid and separator overhead were presented earlier in Table 21. The boiling range of the filtered liquid (0.9°API) was 398°F (IBP) to 622°F at 50 volume percent distilled. The ASTM distillation boiling range of the separator overhead product (24.6°API) was 168°F (IBP) to 670°F end point. As in previous runs, the pressure filtered liquid contained some hydrogenated anthracene oil.

The separator overhead product was contaminated by heavy liquid due to poor level control in the hot separator. This shows up in the low API gravity and high end point of the overhead product.

Sulfur analyses on the liquid products show that the pressure filtered liquid (gas oil) was desulfurized to 0.07 weight percent sulfur in the ebullated bed; but, the separator overhead (naphtha) again was partially desulfurized (0.23 weight percent sulfur). The overhead sulfur content was lower than in previous runs because of the presence of filtered liquid in the overhead product, which is a low sulfur contaminant not normally present in this stream.

Pseudo-DBP analyses ranged from 68 to 70, equivalent in structure to Runs 144-144, -145, and -146 carbon blacks.

No material balance is available on this run because there was no gas analysis.

Single-Stage Operations - Run 177-72: This run was made in Unit 177, which is functionally the same as Unit 144, except that it has a larger reactor diameter of 0.815 inches compared to 0.614 inches for Unit 144 and a total reactor volume of 1,000 cc compared to 400 cc.

It was anticipated that the larger diameter reactor would aid ebullation and prevent slugging. Experiments performed in a 1-inch lucite tube indicated an internal recycle rate of 81,000 cc per hour was needed for good ebullation. In the lucite tube tests, no difficulties were encountered in passing -36 mesh rubber through a bed of 1/16-inch diameter extruded catalyst.

The run was terminated after three hours on stream because of excessive pressure drop in the reactor. No product analyses are available because of the short on-stream time.

Single-Stage Operations - Run 177-73: Run 177-73 was made at 2,250 psig in an effort to prevent slugging in the reactor by compressing the volume of gas flowing through the reactor. Five hours after initiation of rubber feed, the pressure drop across the reactor started to build steadily. The run was terminated after six hours at lined out conditions because of excessive pressure drop across the reactor. Total time on stream was 19 hours.

Only analyses on the separator overhead liquid and the carbon black are available from this run. The ASTM distillation boiling range of the separator overhead product (23.2°API) was 166°F (IBP) to 680°F end point. Again, as in Run 144-146, the overhead product was contaminated with filtered liquid because of poor separation of the reactor products.

Because of the presence of filtered liquid in the overhead product, the sulfur content of the overhead was lower (0.1 weight percent) than observed in Runs 144-145 and -146.

No pseudo-DBP analyses were performed.

Single-Stage Operations - Run 144-156: A successful five-day demonstration run (144-156) of the catalytic H-Rubber process was made feeding ground tire tread peelings. A previous attempt at this type of operation (Run 144-155) was terminated because of mechanical problems before the rubber feed was introduced to the unit. A detailed operating program is presented in Table 23.

OPERATING CONDITIONS

Run 144-156

Period	1	2A	2B	3	4A	4B	5	6
Length of Period, Hrs.	7	5	19	24	8	16	24	24
Catalyst	1/16" Nalco 471 CoMo ----------							
HRI Catalyst Number	2308 ----------							
Reactor Temperature, °F	850 ----------							
Preheater Temperature, °F	830/840 ----------							
Hydrogen Pressure, psig	1000 ----------							
Oil + Rubber Feed, Gms/Hr	830	925	885	876	956	1090	975	922
Rubber Concentration, W %	6		8	10	10	9	10	11
HRI Number (Tread Peelings)	3286 ----------							
Internal Recycle, cc/Hr	20,000 ----------							
External Recycle, V_R/V_{FF}	0	0	∞	∞	∞	5	13	15

TABLE 23

The run was initiated by feeding 50 grams per hour of ground tread peelings. After 12 hours on stream, recycle of pressure filtered liquid was begun. After 22 hours on stream, the rubber feed rate was increased to 100 grams per hour. The unit remained on total recycle for 51 hours before hydrogenated anthracene makeup oil had to be added because of high entrainment of product gas oil in the filtered solids. The run was continued for a total time of 127 hours on rubber feed.

The unit was shut down voluntarily after 5.3 days of operation. The pressure drop across the reactor increased to 100 psig over the length of the run, but this pressure drop did not impair the operation of the unit.

This result is in sharp contrast to earlier attempts to run with ground tire containing two to four percent fibers. In all of the earlier runs, sustained operation could not be achieved because of sudden reactor pressure drop buildups, which occurred within a few hours of introducing the rubber feed.

The major difference between the tire peelings and the ground rubber previously processed is the lack of glass fibers. It is felt that this permitted the successful operation. In all probability, the problem with the glass fibers is specific to the small diameter pilot plants used for this work and would not be a problem in larger equipment.

As expected, the pseudo-DBP absorption number (80-82) for the carbon black from tread peelings was higher than previously obtained from ground whole tires. Tread peelings contain higher reinforcing blacks than the carcass and, therefore, were expected to have a higher DBP number.

Liquid and gas yields were similar to previous catalytic and non-catalytic operation (Table 24), except for the concentration of the sulfur in the gas oil fraction. The gas oil was catalytically desulfurized to 0.07 weight percent sulfur. With non-catalytic operation (discussed later), a hydrotreating step was necessary to bring the gas oil sulfur content down to this level. The naphtha fraction was not catalytically desulfurized.

TABLE 24

SUMMARY OF YIELDS AND OVERALL MATERIAL BALANCES

-24 MESH GROUND TREAD PEELINGS

Period	144-156-2B/3/4A
W %	
CH_4	0.28
C_2H_4	----
C_2H_6	0.37
C_3H_6	0.25
C_3H_8	0.38
C_4H_8	0.28
C_4H_{10}	0.29
C_4 Iso	0.09
C_5H_{10}	0.13
C_5H_{12}	0.14
C_5 Iso	0.10
C_6H_{12}	----
C_6H_{14}	----
C_6 Iso	----
Naphtha	25.8
Gas Oil	(-3.8)
Solids + Entrained Oil	73.4
TOTAL	97.7

The material balance yields (total 97.7 weight percent) for the gas oil recycle portion of the run (51 hours) are listed in Table 24. The gas oil yield indicated was negative, but approximately 50 percent of the solids yield was entrained gas oil which was not separated by filtration.

Table 25 lists inspections on the separator overhead and bottoms liquid products. Periods 3 and 4A inspections were on liquid products from the total recycle portion of the run.

Two-Stage Operations - Run 144-151: Over a seven hour period, the rubber concentration in the oil feed was increased to 14 weight percent (200 Gm/Hr rubber). Both stages were running smoothly when the bottom liquid product control valve plugged with material which had not been completely washed from the unit after a previous operation not connected with the H-Rubber program. The catalyst bed was upset when the plug was blown clear with nitrogen, resulting in the loss of internal recycle flow and subsequent shutdown of the unit.

Since the run was so short, no product analyses were made.

Two Stage Operations - Run 144-152: Run 144-152 was a two-stage run similar to Run 144-151. The first stage was non-catalytic with 850°F reactor temperature. The products from the first stage went to a second stage containing an ebullated catalyst bed (785°F) in which the products were further hydrogenated. Operation was once-through with no external recycle of the gas oil product. The carbon black was separated from the gas oil by pressure filtration.

The unit was on rubber feed for four hours when the differential pressure across the catalytic reactor built to 2,000 psig. The unit was shut down and the catalyst bed was dumped.

A flat, one-inch piece of material was removed from the dumped catalyst bed. This material was later benzene extracted and found to contain about 40 percent soluble material in benzene.

LIQUID PRODUCT INSPECTIONS

Run 144-156

Period	3		4A		6	
Product	Separator Overhead	Pressure Filtered Liquid	Separator Overhead	Pressure Filtered Liquid	Separator Overhead	Pressure Filtered Liquid
Gravity, °API	28.1	1.1	33.3	0.4	39.7	0.5
ASTM Distillation, V %						
IBP, °F	162	404	162	402	152	418
10%	236	506	228	500	220	494
30%	300	580	300	584	292	578
50%	354	642	340	650	334	650
70%	406	---	384	---	372	---
90%	---	---	466	---	422	---
FBP	---	---	592	---	460	---
V % @ 600°F	69	36	---	35	---	---
V % @ 650°F	94	56	---	50	---	---
W % Sulfur	0.63	<0.07	0.78	<0.07	0.86	<0.07

TABLE 25

The remaining solid residue lost no weight on ashing. This ashed material was clearly a mat of glass fibers. This observation was confirmed by microscopic examination of the ashed material.

Two-Stage Operations - Run 144-153: In an effort to prevent the glass fibers from "matting" together and plugging the catalyst bed, the rubber feed was pretreated to remove the glass fibers. The ground rubber feed was elutriated with nitrogen before being fed to the unit. About 50-75 percent of the fine fibers were removed from the rubber.

The catalytic stage again plugged up. The dumped catalyst revealed what looked like small pieces of rubber which were not as elastic as the feed rubber. A sample of this material was analyzed. The material was SBR, but could possibly contain some natural rubber.

Based on a pseudo-DBP number of 70, the carbon black produced in this run was equal in structure to all other carbon blacks made from whole ground tires using catalytic or non-catalytic operations. There were no liquid or gas analyses for Run 144-153.

Discussion of Results

The major finding of the catalytic work was that carbon black of recyclable quality could be removed from the ground tires while simultaneously producing low sulfur oil.

The bench-scale system operated quite satisfactorily with -24 mesh ground tire tread peelings, which were essentially fiber free. However, the operability of the bench-scale catalytic system was very disappointing with the -24 mesh ground tires containing glass fibers. The continued bed plugging problems were obviously caused by interaction of the partially converted rubber particles, the catalyst particles, and the glass fibers to produce a slugging bed.

In all cases where bed plugging was observed, a mat of glass fibers was found at the catalyst zone outlet. Partially converted rubber was found mixed with the catalyst particles to make up plugs that were pushed up against the top of the zone.

The two-stage system had little success in improving on-stream times for the catalyst system. The problems caused by the glass fibers were not resolved since the fibers carried over into the second stage without being changed.

The rubber and catalyst system were examined under non-reaction conditions in a 5/8-inch inside diameter lucite tube model of the system. It appears that the rubber particles would normally pass through the ebullated catalyst bed. However, on occasion, a slug would form above the inlet of the bed. These slugs were quite stable and could not be dislodged by tapping the side of the tube, which is the normal procedure. It seems, in fact, that the slugs were jammed between the reactor walls and held there in part by the elasticity of the rubber. Perhaps, the formation of slugs in the lucite tube system was analogous to what was occurring in the actual reactor. In a 1.0-inch inside diameter lucite tube, no slugs were formed.

These observations indicate that the operating difficulties were more a function of the small diameter of the reactor used than the reaction system. In addition, the use of screens, which is necessary in reactors of this diameter, provided a trap for glass fibers. This problem would be eliminated in larger equipment.

NON-CATALYTIC PILOT PLANT OPERATIONS

General

A total of four non-catalytic pilot plant runs were made. The operating program for these runs is summarized in Table 26.

Unit Description and Procedure

The same single-stage unit and procedures that were used for the catalytic work were used without any changes for the non-catalytic experiments. A simplified flow sheet of this unit was presented previously in Figure 3.

Results

Run 144-147: This run was made without catalyst to determine product quality and operational problems involved with non-catalytic hydrogenation of rubber (-36 mesh, HRI 3219) at 800°F and 850°F and 1,000 psig. No recycle of filtered liquid was attempted since the run was exploratory in nature.

The run was shut down voluntarily after 23 hours at 800°F followed by 11 hours at 850°F, so that the unit could be turned around for a run using 1/32" HDS-1441 catalyst.

The reactor was opened and found to be clean. A small amount of gummy material was found on the screen at the top of the reactor.

OPERATING PROGRAM

NON-CATALYTIC PILOT PLANT OPERATIONS

Run	144-147	144-149	144-150	144-154
Reactor Temperature, °F	800-850	850	850	850
Hydrogen Pressure, psig	1000	1000	1000	1000
Total Feed Rate, Diluent Oil + Rubber, Gms/Hr	900	900	1535-3077	2800
Rubber Concentration, W %	11.0	11.0	11.8-13.3	11.8-14.8
Rubber Size, Mesh	-36	-36	-36, -24 As Received	-24
HRI Number, Rubber	3219	3219	3219, 3221	3219
Use of Filtered Liquid Product as Diluent Oil	No	Yes	Yes, No	Yes
Internal Recycle Rate, cc/Hr	30,000	30,000	45,000	45,000
Length of Run, Hrs	34	56	120	160

TABLE 26

Material balances for the three separate periods within the 34-hour operation are listed in Table 27. Only one gas sample was taken during the run (Period 1). The gas yields from this sample were used in the material balance for the three periods. Overall material balances ranged from 96.7 to 97.8 weight percent.

These overall balances do not really give significant information in terms of yields on rubber feed since the rubber represented only 11 percent of the total feed. They are useful only as a measure of the performance of the experimental system.

The carbon black, which was filtered from the hot separator bottoms product, was evaluated for both chemical and compound testing and to characterize the black. A high structure, semi-reinforcing black (ASTM N-765) was tested, along with the HRI produced carbon black.

The test results are presented in the Product Evaluations section of this report. Included in this section are the results of tests made on blacks produced during catalytic operation (Run 144-146).

The results of the product evaluations indicated that:

1. The samples from catalytic and non-catalytic operation were similar in both chemical properties and in reinforcement of natural rubber.

2. The samples exhibited good reinforcement of natural rubber and should have commercial value.

As a check on HRI's pseudo-DBP analysis, Uniroyal's DBP absorption number was 67, while the HRI pseudo-DBP number was 65-67.

Run 144-149: This run was a 56-hour non-catalytic operation at 850°F reactor temperature and 1,000 psig reactor pressure. The rubber feed (100 Gms/Hr) was made up of -36 mesh ground rubber which was screened from the rubber received from Uniroyal. The hydrogen, slurry oil, and rubber feed were put

TABLE 27

EXPERIMENTAL MATERIAL BALANCES AND YIELD SUMMARY

Run 144-147

Period	1	2A	2B
Hours on Stream	0-16	16-23	23-34
W % on Total Feed			
CH_4	0.07		
C_2H_4	----		
C_2H_6	0.03		
C_3H_6	----		
C_3H_8	0.22		
C_4H_8	0.17		
C_4H_{10}	0.14		
C_4 iso	0.05		
C_5H_{10}	0.05		
C_5H_{12}	0.09		
C_5 iso	0.06		
C_6H_{12}	----		
C_6H_{14}	----		
C_6 iso	----		
Naphtha	0.45	0.91	1.73
Gas Oil	91.37	89.09	89.95
Solids + Entrained Oil	4.00	6.15	5.28
Material Balance Closure, W %	96.70	97.03*	97.84*
Feed			
W % Rubber	11	11	11
W % Diluent Oil (L-279)	89	89	89

Only one gas analysis was taken. This was during Period 1.

* The total material balances for Periods 2A and 2B use the gas analysis from Period 1.

through the preheater at 800°F, along with internal recycle oil. Recycle of the filtered liquid bottoms product and hydrogenated anthracene makeup oil at ratios of 9 to 1 and 11.7 to 1 was accomplished during the last 44 hours of the run. It was not possible to completely eliminate the makeup oil requirements because of the amount of oil left with the filter cake.

The run was voluntarily terminated after 56 hours on stream in order to make a catalytic run in a larger diameter ebullated bed reactor which had become available. The reactor was not opened because the non-catalytic run was continued as Run 144-150 when the catalytic run was completed.

A material balance has been provided for Period 144-149-3 in Table 28. Although the material balance closure is essentially high, it points out that the amount of C_1-C_3 gas produced was only 2.6 weight percent, while the naphtha yield was 16.2 weight percent on a total feed that was 93.7 weight percent rubber.

Table 29 lists analyses on gas oil and naphtha products. The inspections do not represent final liquid products from rubber cracking because the gas oil contains hydrogenated anthracene makeup oil and the separator overhead in this run was contaminated by the gas oil product due to improper level control in the hot separator.

Table 30 lists the actual versus theoretical carbon black yields obtained during this run. The theoretical yield was calculated from the sum of the carbon and inorganic solids in the original rubber. During the initial period (144-149-1), the concentration of rubber in the feed slurry was still increasing to a steady rate of 100 grams per hour of rubber to the reactor. The actual yield was, therefore, lower than the theoretical yield based on 100 grams per hour of rubber feed. For the remainder of the run at 100 grams per hour, the carbon was completely sprung and theoretical yields were obtained. Pseudo-DBP numbers ranged from 66 to 70, similar to carbon blacks previously produced.

TABLE 28

EXPERIMENTAL MATERIAL BALANCES AND YIELD SUMMARY

NON-CATALYTIC HYDROGENATION OPERATIONS

Run 144-149

Period	3
Hours on Stream	36-56
W / on Total Feed	
CH_4	0.61
C_2H_4	----
C_2H_6	0.48
C_3H_6	----
C_3H_8	1.52
C_4H_8	1.29
C_4H_{10}	0.85
C_4 iso	0.29
C_5H_{10}	0.39
C_5H_{12}	0.51
C_5 iso	0.39
C_6H_{12}	----
C_6H_{14}	----
C_6 iso	----
Naphtha	16.17
Cas Oil	34.73
Solids + Entrained Oil	56.89
Material Balance Closure, W /	114.12
Feed	
W / Rubber	93.7
W / Slurry Oil	6.3

LIQUID PRODUCT INSPECTIONS

Run 144-149

Period	1		2		3	
Product	Naphtha	Gas Oil	Naphtha	Gas Oil	Naphtha	Gas Oil
Gravity, °API	-0.4	-0.6	8.2	-0.4	29.3	-0.1
ASTM Distillation, V %						
IBP, °F	360	428	200	396	150	370
10%	480	500	260	502	248	504
30%	560	594	412	580	308	586
50%	612	650	514	636	346	650
70%	---	---	626	---	386	---
90%	---	---	---	---	468	---
FBP	---	---	---	---	704	---
% @ 600°F	46	33	65	37	94	34
% @ 650°F	67	50	77	56	96	50
Sulfur, W %	0.35	0.16	0.35	0.34	0.38	0.28

TABLE 29

COMPARISON OF ACTUAL TO THEORETICAL CARBON BLACK YIELDS

NON-CATALYTIC HYDROGENATION OPERATIONS

Period	Temp. °F	Hydrogen Pressure psig	Length of Operation Hrs	Rubber Rate, G/Hr	Vol. Filtered Oil / Vol. Makeup Oil	Catalyst	Carbon Black Yields, Gms. Carbon Black/ Gms. Rubber	
							Actual	Theoretical
144-149-1	850	1000	12	100 HRI 3219, -36 Mesh	1.3	--None--	28	36
144-149-2	850	1000	24	100 HRI 3219, -36 Mesh	9.1	--None--	40	36
144-149-3	850	1000	20	100 HRI 3219, -36 Mesh	11.7	--None--	36	36

TABLE 30

Run 144-150: This run was started up using the same reactor as used in Run 144-149. The detailed operating program is given below.

Period	1B	2C	3B	4B	5B
Hours on Stream	12-24	36-48	60-72	84-96	108-120
Reactor Temp., °F	850	----------	----------	----------	----------
Preheater Temp., °F	800	850	850	850	850
Hydrogen Pressure, psig	1000	----------	----------	----------	----------
Catalyst	None	----------	----------	----------	----------
Oil + Rubber Feed, Gms/Hr	1700	1535	3041	3005	3077
Rubber Concentration, W %	11.8	13.0	13.2	13.3	13.0
	(-36 Mesh)	--------		(as is)	------
HRI Number	3219	----------		3221	--------
Internal Recycle, cc/Hr	45,000	----------	----------	----------	----------
Flow of Feed	Through Preheater	----------	----------	----------	----------
Recycle of Pressure Filtered Liquid	Yes	No	No	No	No

Several variables were studied in Run 144-150 at 1,000 psig hydrogen pressure. In Period 1B at 800°F, a higher rubber rate (200 Gms/Hr) than previously attempted was charged and the only operating difficulty encountered was the long time it took to pressure filter the separator bottoms. It was believed at that time that unconverted rubber was plugging the filter pores. Benzene extraction of the carbon black product from Period 1B revealed no signs of unconverted rubber (carbon black passed through a 100 mesh screen) and the pseudo-DBP number was 72, again indicating no rubber contamination. It was later determined that the filter could not handle the large cakes at these higher rubber rates. The high loading resulted in the long filtration times.

In Period 2C, the preheater temperature was raised to 850°F to enhance rubber conversion and the unit was put on a once-through operation with hydrogenated anthracene oil as the carrier. No operating difficulties were encountered.

The rubber rate was increased to 400 Gms/Hr with once-through operation in Period 3B. Again, no operating problems were encountered. The rubber feed was switched from -36 mesh to rubber

as received from Uniroyal (-24 mesh) in Period 4B. Operation was smooth.

The last operation in Run 144-150 was made using a Kuwait light gas oil (508-675°F boiling range) as the slurry oil instead of anthracene oil (L-279). On mixing the rubber (HRI 3321 as received from Uniroyal) with the Kuwait oil (14 weight percent rubber concentration), the rubber did not swell as when anthracene oil was used and settled out immediately in the mixing vessel leaving a clean liquid above the settled rubber. As a comparison, a solution of anthracene oil containing 14 weight percent rubber has a consistency of thick mud throughout the solution.

On charging the rubber-Kuwait oil solution to the charge pot, the mixing action of the stirrer kept the solution well mixed and no pumping problems were encountered in feeding the solution to the reactor. The run was voluntarily shut down after this experiment.

A summary of yields and overall material balances for each period are listed in Table 31. These overall material balances ranged from 96.8 to 101.6 weight percent.

Complete inspections on the liquid products are presented in Table 32. It should be noted again that the liquid products are not made only from rubber cracking, but contain hydrogenated anthracene slurry oil.

As in Run 144-149, the actual carbon black yield (28%) was lower than the theoretical yield based on 200 Gms/Hr of rubber during the initial period (144-150-1B) because of a low rubber concentration in the charge pot. For the remainder of the run, actual yields were close to theoretical yields (36%) indicating complete disengagement of the carbon black from the rubber. This information is tabulated in Table 33.

Carbon blacks produced in Periods 144-150-4B and -5B were tested and evaluated by performing both chemical and physical tests on rubber compounds made from HRI carbon blacks and a commercial highly reinforcing black (IRB #3).

TABLE 31

EXPERIMENTAL MATERIAL BALANCES AND YIELD SUMMARY

NON-CATALYTIC HYDROGENATION OPERATIONS

Run 144-150

Period	2C	3B	4B	5B
Hours on Stream	36-48	60-72	84-96	108-120
W % on Total Feed				
CH_4	0.11	0.06	0.05	0.06
C_2H_4	----	----	----	----
C_2H_6	0.09	0.04	0.04	0.06
C_3H_6	----	----	----	----
C_3H_8	0.27	0.20	0.19	0.29
C_4H_8	0.33	0.20	0.23	0.19
C_4H_{10}	0.13	0.05	0.06	0.09
C_4 iso	0.04	0.02	0.02	0.03
C_5H_{10}	0.26	0.15	0.15	0.09
C_5H_{12}	0.13	0.13	0.06	0.05
C_5 iso	0.10	0.10	0.05	0.04
C_6H_{12}	0.01	----	----	----
C_6H_{14}	----	----	----	----
C_6 iso	----	----	----	----
Naphtha	1.17	0.98	0.40	1.11
Gas Oil	82.80	90.00	85.86	88.17
Solids + Entrained Oil	11.40	9.67	9.95	9.36
Material Balance Closure, W %	96.84	101.60	97.06	99.54

LIQUID PRODUCT INSPECTIONS

Run 144-150

Period	2C		3B		4B		5B	
Product	Naphtha	Gas Oil	Naphtha	Gas Oil	Naphtha	Gas Oil	Naptha	Gas Oil
Gravity, °API	25.6	-0.7	36.5	0.0	40.7	-0.5	50.5	30.8
ASTM Distillation, V %								
IBP, °F	140	396	131	428	130	352	120	368
10%	252	520	191	516	196	496	172	522
30%	298	592	264	596	260	590	228	580
50%	340	---	300	650	286	612	260	620
70%	392	---	336	---	318	---	296	650
90%	660	---	424	---	376	---	334	---
FBP	---	---	710	---	570	---	518	---
% @ 600°F	86	33	93	31	---	---	---	40
% @ 650°F	89	49	94	50	---	---	---	70
Sulfur, W %	0.39	0.08	0.31	0.17	0.68	0.15	0.45	1.71

TABLE 32

COMPARISON OF ACTUAL TO THEORETICAL CARBON BLACK YIELDS

NON-CATALYTIC HYDROGENATION OPERATIONS

Period	Temp. °F	Hydrogen Pressure psig	Length of Operation Hrs	Rubber Rate, G/m	Vol. Filtered Oil / Vol. Makeup Oil	Catalyst	Carbon Black Yields, Gms. Carbon Black/ Gms. Rubber	
							Actual	Theoretical
144-150-1B	850	1000	12	200 HRI 3219, -36 Mesh	No Make Feed, All Recycle	--None--	28	36
144-150-2C	850	1000	12	200 HRI 3219, -36 Mesh	0	--None--	39	36
144-150-3B	850	1000	12	400 HRI 3219, -36 Mesh	0	--None--	38	36
144-150-4B	850	1000	12	400 HRI 3221, As Received	0	--None--	35	36
144-150-5B[1]	850	1000	12	400 HRI 3221, As Received	0	--None--	36	36

1. Kuwait Light Carrier Oil (HRI 3051)

TABLE 33

Results of these evaluations indicated that:

1. The HRI produced black exhibited reinforcement in both natural rubber and styrene butadiene rubber.

2. Reinforcement was similar to previously tested catalytically and non-catalytically produced blacks.

A complete listing of the test results are presented in the Product Evaluations section of this report.

Sulfur balances were calculated for Periods 144-150-2C, -3B, -4B, and -5B and are given in Table 34. Accountability ranged from 94 to 111 weight percent and the distribution suggested that 50 to 85 percent of the sulfur originally in the rubber came out in the carbon black.

Run 144-154: Run 144-154 was a seven-day demonstration of the H-Rubber process with no catalyst in the reaction zone and with recycle of the filtered gas oil product as slurry oil. The conditions for this run were as follows:

Periods	1B	2B	3B	4	5	6	7
Time on Stream, Hrs.	12-24	36-48	60-72	72-96	96-120	120-144	144-160
Reactor Temp., °F	850	----------					
Hydrogen Pressure, psig	1000	----------					
Catalyst	None	----------					
Rubber Feed, Gms/Hr	183	333	400	400	400	386	375
Rubber Concentration, W %	11.8	14.0	13.0	13.6	14.8	13.2	14.3
HRI Number (Rubber)	3221	(As Received)	----------				
Recycle Ratio, V_R/V_{FF}	3	4	∞	∞	∞	31	∞
Internal Recycle, cc/Hr	45,000	----------					

The first 2.5 days were used to bring the unit onto totally internally generated recycle oil filtered from the hot separator bottoms as the recycle slurry oil for the rubber. The next 56 hours were

SULFUR BALANCES (BASED ON 100% OVERALL MATERIAL BALANCES)

Run 144-150

Period	Sulfur in Feed Gms/Hr		Sulfur in Product, Gms/Hr				Sulfur in Carbon Black / Sulfur in Rubber	Sulfur Balance W%
	Rubber	Oil	Pressure Filtered Liquid	Overhead Liquid	Carbon Black	Gas		
2C	3.30	1.74	1.15	0.07	2.80	0.70	0.85	94
3B	6.60	3.43	4.90	0.09	3.28	1.18	0.50	94
4B	5.72	3.40	4.27	0.09	4.72	1.03	0.82	111
5B	5.72	50.60	49.64	0.15	3.40	1.00	0.59	104

TABLE 34

lined out on total recycle and a material balance was established around the unit. During the last two days of operation, some hydrogenated anthracene makeup oil was inadvertently added and this period is not included in the material balance period.

The unit was shut down voluntarily after seven days of operation. No operating difficulties were encountered during the run. A small deposit (17.0 grams) was found in the reactor. It consisted of about 90 percent combustible and 10 percent non-combustible materials. No analyses were obtained on the non-combustible portion.

Detailed inspections were carried out on the gas oil and naphtha fractions which represented 42.6 and 16.7 weight percent on ground tire feed, respectively.

Table 35 includes the inspections on the gas oil and naphtha. The products were fractionated into several cuts and detailed analyses were performed.

A PONA* analysis for the 200-350°F fraction of the naphtha is given in Table 36. Overall material balanced yields were worked out for this operation and are presented in Table 37.

Conventional hydrotreating of the naphtha and gas oil products from Run 144-154 was carried out at mild desulfurization conditions in a fixed bed reactor. The operating conditions are summarized below:

Run Number	148-338	148-339
Length of Run, Hrs.	10	10
Reactor Temperature, °F	700	700
Hydrogen Pressure, psig	1020	1010
Catalyst	Am. Cy. HDS-1441	Am. Cy. HDS-1441
HRI Catalyst Number	3161	3161

* Paraffin, Olefins, Naphthenes, Aromatics

SUMMARY OF INSPECTIONS OF H-RUBBER PRODUCT FRACTIONS

Run 144-154

Weight % on Rubber Feed	16.7				42.6				
Description	Naphtha				Gas Oil				
Fraction, °F	Total	I-200	200-350	350+	Total	I-400	400-650	650-975	975+
Volume %	100.0	8.3	67.7	24.0	100.0	4.0	41.7	41.3	13.0
Gravity, °API	35.9	62.9	44.0	27.6	1.4	25.0	11.1	-2.6	-28.8
Sulfur, W %	0.69	0.51	0.54	1.43	0.49	0.60	0.58	0.50	0.60
Carbon, W %	89.10	84.54	86.95	85.40	90.00	85.89	90.10	90.40	92.40
Hydrogen, W %	8.29	14.33	12.29	11.34	7.90	13.27	9.01	7.39	5.39
Flash Point, °F	70				265				
Fire Point, °F	85				305				
Nitrogen, ppm	1911	715	1348	3518	4955	992	3452	4933	6123
Aniline Pt., °F		78	46	33					
Bromine No., cgs/Gm		NES	3.16						
Viscosity, SUS @ 122°F	27				124				
Pour Point, °F					0	NES	-15		
ASTM Color			L1.0						
ASTM Distillation									
IBP/10	164/226	NES	190/228	NES		NES	460/494		
30	278		256				520		
50	306		276				566		
70	340		298				608		
90	390		336				658		
EP	493		382				692		

NES = Not Enough Sample

TABLE 35

TABLE 36

ANALYSIS OF THE 200-350°F NAPHTHA FRACTION

NON-CATALYTIC HYDROGENATION OPERATIONS

Run 144-154

	Liquid %
Mass Spectrometer Analysis*	
Paraffins	12.02
Napthenes	31.52
Aromatics	34.67
Dicycloparaffins	21.79
	100.00
Aromatic Distribution	
Benzene	2.91
Toluene	9.65
Xylene	13.78
C_9 Aromatics	4.73
C_{10} Aromatics	3.37
C_{11} Aromatics	0.23
	34.67
F.I.A. Analysis	
Aromatics	32.4
Olefins	37.4
Saturates	30.2
	100.0

* The high napthene and di-napthene content reflects high concentrations of olefins and should be integrated to the F.I.A. analysis achieved on the sample.

TABLE 37

SUMMARY OF YIELDS

NON-CATALYTIC HYDROGENATION OPERATIONS OF -24 MESH GROUND TIRES

Run 144-154

OPERATING CONDITIONS

Temperature, °F	850
Hydrogen Pressure, psig	1000
Rubber Feed Rate, Lbs/Hr/Ft^3 Reactor	62.5
Diluent/Rubber Weight Ratio	0.
Hydrogen Rate, SCF/Ton Rubber	34,000
Hydrogen Consumption, SCF/Ton Rubber	3560

YIELDS

	W % FF	Gravity °API	Sulfur W %
H_2S	0.3		
NH_3	---		
C_1	0.4		
C_2	0.3		
C_3	1.8		
C_4	1.6		
C_5-200°F	2.2	76.6	0.51
200-350°F	8.1	44.0	0.54
350-650°F	22.3	14.4	0.50
650-975°F	19.3	-2.6	0.50
975°F+	7.6	-28.8	0.60
Solids	37.0	----	2.50
TOTAL	100.9		

Feed	Pressure Filtered Liquid (Gas Oil)	Separator Overhead (Naphtha)
L-No.	318	319
Feed Rate, Gms/Hr	255	164

Each hydrotreating run was 10 hours in length and no operational problems were encountered.

Detailed analyses of the hydrotreated products are summarized in Table 38.

The desulfurization of naphtha inspections indicate an increase in API gravity, a volumteric decrease in the 200-350°F fraction, and an increase in the IBP-200°F and 350°F+ fractions.

Catalyst desulfurization of the gas oil produced a lighter product (1.4°API versus 9.0°API) with a quantitative decrease in the 650-975°F fraction and an increase in the IBP-400°F fraction. The gas oil was desulfurized to 0.22 weight percent sulfur.

Catalytic desulfurization of the naphtha fraction from Run 144-154 reduced the sulfur content from 0.69 to 0.29 weight percent. In an effort to improve the naphtha product sulfur concentration, the hydrotreating operation was repeated at less severe conditions to increase naphtha residence time in the reactor. The results listed in Table 39 show little improvement in sulfur level.

Discussion of Results

The non-catalytic hydrogenation of ground rubber tires seems to offer great potential as a means for disposing of ground tires. Unit operability throughout the test series was quite good.

SUMMARY OF HYDROTREATING RESULTS OF H-RUBBER PRODUCT FRACTIONS

Run	148-339				148-338				
Description	Hydrotreated Naphtha				Hydrotreated Gas Oil				
Fraction, °F	Total	I-200	200-350	350+	Total	I-400	400-650	650-975	975+
Volume %	100.0	15.7	43.0	41.5	100.0	25.7	40.0	22.0	12.3
Gravity, °API	36.2	59.3	45.1	20.4	9.0	34.2	18.4	2.7	-11.2
Sulfur, W %	0.27	<0.07	<0.07	0.24	0.22	<0.07	<0.07	0.19	0.49
Carbon, W %		85.11	87.14	89.0		87.08	89.1	90.8	90.6
Hydrogen, W %		14.07	12.90	10.99		12.19	10.18	8.55	6.86
Flash Point, °F	60				200				
Fire Point, °F	75				225				
Nitrogen, ppm	747	292	335	1051	1730	1534	1835	3033	4808
Aniline Pt., °F									
Paraffins									
Olefins									
Naphthenes									
Aromatics									
Bromine No., cgs/Gm		3.9	2.8	1.0			9.82		
Viscosity, SUS @ 122°F	52				107				
ASTM Distillation									
IBP			233				450		
10			244				514		
30			274				554		
50			294				608		
70			314				624		
90			358				648		
EP			400				692		

TABLE 38

TABLE 39

SUMMARY OF HYDROTREATING RESULTS OF H-RUBBER NAPHTHA

Run	148-339	148-340
CONDITIONS		
Length of Run, Hours	10	10
Reactor Temperature, °F	700	625
Hydrogen Pressure, psig	1000	1000
Catalyst	1/32" HDS-1441	1/32" HDS-1441
HRI Catalyst Number	3161	3161
Feed	Separator Overhead (Naphtha)	Separator Overhead (Naphtha)
HRI Feed Number	L-318	L-321
Space Velocity, V/hr/V	1.19	0.76
Hydrogen Rate, SCF/Bbl	~4000	1670
PRODUCT INSPECTIONS		
Gravity, °API	36.2	36.9
Sulfur, W %	0.29	0.19

Obviously, the fluidization problems that were encountered during catalytic operation due to the interaction of catalyst particles, rubber particles, and glass fibers were absent. Without the catalyst in the small diameter reactor, it was possible to feed -24 mesh rubber as received with no fiber elimination step.

As far as could be determined, there was no difference in the quality of the carbon obtained in these runs and that obtained in the catalytic operation.

The major difference in the two operations in terms of product quality was the concentration of sulfur in the gas oil product fraction which represents about 40 percent of the yield based on ground rubber fed in. In the non-catalytic operation, this value was usually in the 0.5 to 0.7 weight percent range, while, with catalyst, it was generally less than 800 ppm. The naphtha fraction from both operations had a sulfur content of about 0.5 to 0.7 weight percent. Since this material immediately enters the vapor phase upon being cracked from the rubber molecules, the catalyst is not effective in treating it.

GENERAL DISCUSSION OF RESULTS

The H-Rubber experimental program progressed from a series of process variable screening studies in a batch stirred reactor to experimentation in continuous, catalytic and non-catalytic, ebullated bed units. The experimentation culminated in a 6.7 day demonstration of the non-catalytic ebullating bed process with slurry oil recycle. A commercial flow sheet with economics was developed from the product yields and inspections from this demonstration run.

The stirred autoclave runs screened the important variables and produced a range of process conditions necessary for a successful continuous process with a minimum of processing difficulties. The autoclave results indicated the following

slate of conditions would give complete reaction of the rubber to useful gas, liquid and solid products.

Reactor Temperature, °F	660 to 850
Pressure, psig	500 to 2,000
Catalyst	None, CoMo or NiMo
Slurry Oil	Anthracene

Not only did the autoclave experiments produce a set of process conditions that would totally react the rubber, but they also provided good indications of expected product quality. It was found that carbon black product quality was essentially constant and independent of the process conditions used to "spring" it from the rubber. Gas yields were found solely to be a function of cracking temperature. Differentiation of liquid product quality was not possible because of contamination of the oil produced from the rubber with the slurry oil. It was determined that the slurry oil was necessary to totally react the rubber and "spring" the carbon black at the conditions studied.

Based on the stirred autoclave results, a catalytic ebullating bed program was set up which included the following process conditions:

Reactor Temperature, °F	800 to 850
Pressure, psig	1,000
Catalyst	Cobalt Molybdate on alumina
Slurry Oil	Hydrogenated anthracene

The high level of reactor temperatures was chosen for the catalytic studies to ensure complete reaction of the rubber. Residence time in the ebullated bed reactor was lower than in the stirred autoclave and incomplete reaction could cause slugging and, eventually, plugging of the catalyst bed.

Though no pressure effects were noted during the autoclave studies, it was desirable to maintain a high hydrogen partial pressure of 1,000 psig in the reactor to prevent possible coke formation. Cobalt molybdate on alumina catalysts were chosen because of their excellent hydrogenation capabilities.

Hydrogenated anthracene oil was employed as the slurry oil because it contained more hydrogen than regular anthracene oil and it was thought that this would be more similar in molecular structure to oil derived from the ground rubber tires.

The catalytic ebullating bed program produced only one totally operationally successful run. This run employed tire tread peelings without glass fibers. But the catalytic program did develop answers as to the causes of the plugging of the catalyst bed, and did produce products for analytic inspection and eventual comparisons with non-catalytically made products.

The problem of the plugged catalyst bed caused by the interaction of the partially converted rubber particles, the catalyst particles, and the glass fibers was solved only by using fiber free tire tread peelings. A 5.3 day continuous run using peelings confirmed that rubber could be totally reacted to gas, oil, and carbon black products using an ebullating bed. Fluidization tests performed in plastic tubes indicated that larger diameter reactors would not be prone to this interaction of glass fibers, catalyst, and rubber particles.

The gas oil was desulfurized to < 0.07 weight percent sulfur and the naphtha was not desulfurized due to low residence time in the reactor.

In light of the problems caused by the glass fibers in the catalytic runs, it was decided to react the rubber using the ebullating bed process without catalyst. The stirred autoclave runs indicated that catalyst was not necessary to react the rubber so that the carbon could be recovered. The autoclave runs also showed that the catalyst had no effect on the quality of the carbon black produced.

Process conditions similar to the catalytic ebullated bed runs were chosen for the non-catalytic program. These were:

Reactor Temperature, °F	800-850
Pressure, psig	1,000
Slurry Oil	Hydrogenated Anthracene

The first two runs of the non-catalytic program were made to establish operability of the unit and feasibility of recycle of filtered slurry oil. Both of these objectives were achieved with runs of 34 and 56 hours which were shut down voluntarily. A variable study convering 120 hours of continuous operation was then made. The study achieved rubber throughput rates of from 30 to 60 pounds-per-hour-per-cubic-foot of reactor, investigated rubber particle sizes of -24 mesh and -36 mesh, and used a Kuwait light gas oil as slurry oil for approximately 24 hours. Operability remained good over these ranges of variables. Carbon product quality was equivalent to catalytic operation and remained constant for the variable ranges studied.

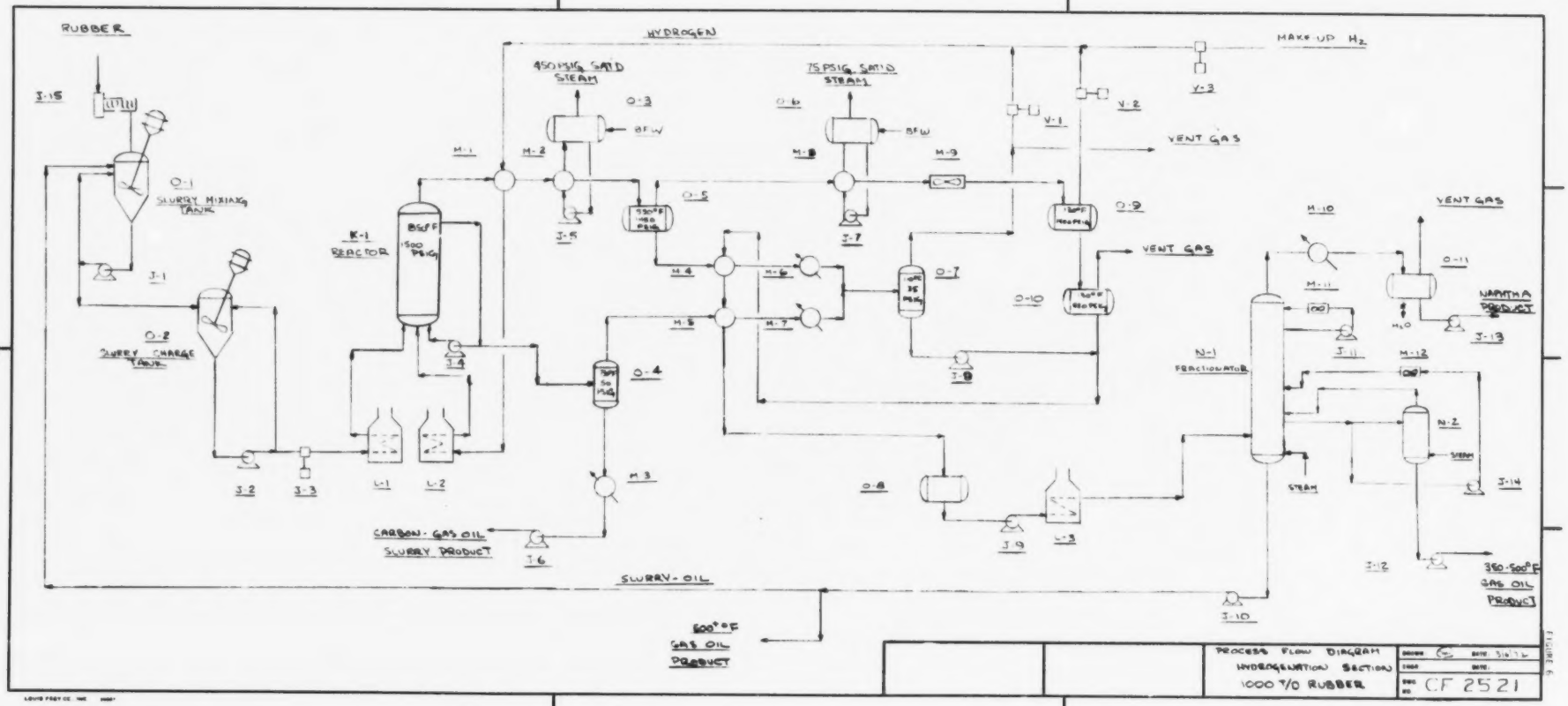
The successful non-catalytic program was culminated with a 6.7 day non-catalytic demonstration run with 56 hours on total recycle of filtered slurry oil.

Operationally, the run was a complete success. Product yields were obtained for the 56 hour total recycle period. A commercial design and economics were based on these yields. Carbon black product quality was not as good as previously produced from catalytic and non-catalytic runs. Tests indicated that a residue was left on the carbon black which affected the bonding characteristics of the black with rubber during curing.

Several experiments were performed on the carbon black product which raised the pH of the black and volatilized the residue left on the black. The quality of the black was significantly improved, but still was not as good as blacks made in Runs 144-146, -147, and -150. The poor quality of the black produced catalytically from tread peelings is believed to also be caused by this residue.

PROPOSED COMMERCIAL FLOW SHEET

On the basis of the data collected during the non-catalytic Run 144-154, the commercial process flow sheet for the hydrogenation section of the H-Rubber plant was prepared and is presented in Figure 6.


RUBBER
HYDROGEN
MAKE-UP H_2
450 PSIG SATD STEAM
75 PSIG SATD STEAM
BFW
VENT GAS
I-15
O-1
SLURRY MIXING TANK
J-1
O-2
SLURRY CHARGE TANK
K-1
REACTOR
850°F 1500 PSIG
J-2
J-3
L-1
L-2
J-4
J-5
J-6
J-7
J-8
J-9
J-10
M-1
M-2
M-3
M-4
M-5
M-6
M-7
M-8
M-9
M-10
M-11
M-12
O-3
O-4
O-5
O-6
O-7
O-8
O-9
O-10
O-11
V-1
V-2
V-3
N-1
FRACTIONATOR
N-2
STEAM
H_2O
NAPHTHA PRODUCT
J-13
J-14
J-12
380-500°F GAS OIL PRODUCT
CARBON-GAS OIL SLURRY PRODUCT
T-6
SLURRY-OIL
600°F GAS OIL PRODUCT
PROCESS FLOW DIAGRAM
HYDROGENATION SECTION
1000 T/D RUBBER
DRAWN
DATE 3/9/56
CHKD
DATE
DWG NO CF 2521

The -24 mesh rubber is mixed with recycle slurrying oil in vessel O-1 and is transferred to slurry feed tank O-2. A slurry consisting of six parts by weight of oil to one part of rubber is used. The oil-rubber slurry is pumped to approximately 1,700 psig, preheated in heater L-1, and fed to the bottom of the ebullating reactor K-1. A portion of the liquid withdrawn from reactor K-1 is recycled by means of pump J-4 to maintain ebullation inside the reactor. The reactor, which is also fed with preheated hydrogen, is operated at 850°F and a total pressure of 1,500 psig, which provides a hydrogen partial pressure of 1,000 psig. Rubber is fed to the reactor at a rate of 62.5-pounds-per-hour-per-cubic-foot reactor.

Inside the reactor, the rubber is converted to hydrocarbon gases, naphtha, gas oil, and carbon.

The vapor effluent leaving reactor K-1 is partially cooled in exchanger M-1 by preheating hydrogen, which is recycled back to the reactor. It is then further cooled in M-2 to about 550°F by generating 450 psig steam and passed to flash drum O-5. The condensates collected in O-5 are then cooled in exchangers M-4 and M-6 and collected in drum O-7.

The vapors leaving O-5 are cooled in exchanger M-8 by generating 75 psig steam and finally cooled to 130°F in air cooler M-9. Condensates collected from this stream in O-9 are then flashed to 550 psig in flash drum O-10. Part of the hydrocarbon gases produced in the plant are vented from this drum.

The hydrogen stream leaving drum O-9 is recompressed, joined with makeup hydrogen from V-3 and recycled back to the reactor.

The net carbon-liquid oil stream leaving reactor K-1 is flashed to 50 psig in drum O-4 to provide a carbon-oil stream consisting of 50 weight percent oil and 50 weight percent carbon.

Since the carbon produced from the rubber is extremely fine, the slurrying oil and a part of the oil produced are separated by vaporizing this oil rather than using a mechanical means for separating the carbon from the oil. It is envisioned that the carbon-oil slurry leaving drum O-4 would be the product sold to

rubber manufacturing companies. Since, in the manufacture of rubber tires, the carbon, as well as other ingredients, are slurried with oil, this product will provide this slurrying oil. Carbon from other sources can be added to this slurry to provide the proper carbon-oil mix for the tire manufacture.

The vapors leaving drum 0-4 are cooled in exchangers M-5 and M-7 to 110°F and flashed in drum 0-7 to 35 psig. Dissolved hydrogen, which is recovered in 0-7, is recompressed in V-1 and passed into the recycle hydrogen stream. A portion of this stream is vented to remove additional light hydrocarbon gases from the system. The liquids collected in drums 0-7 and 0-10 are then fractionated in fractionator N-1 to provide the crude naphtha product and a 350-500°F gas oil product. Most of the 500°F+ oil leaving the bottom of N-1 is recycled back to 0-1 as slurrying oil. A small portion is withdrawn as additional gas oil product.

Table 40 presents the yields from the plant and is based on laboratory experimental results. The naphtha and solids-free gas oil produced contains approximately 0.5 weight percent sulfur. The naphtha can be sold to the refinery for further refining. The gas oil can be sold either as a low sulfur fuel oil or it can be sold to the refinery for further processing to petroleum products. It is conservatively estimated that these products should be worth $3.00 per barrel.

Table 41 presents the material balance for the plant. As previously mentioned, the quantity of hydrocarbon gases produced is relatively small and it would be more economical to sell these gases to the refinery. The refinery can remove the hydrogen sulfide in their existing equipment and convert the hydrogen sulfide to lump sulfur by the Claus process. If a separate Claus system to remove the hydrogen sulfide and convert it to lump sulfur is installed in the rubber plant, the capital investment for this sytem will be approximately $275,000.

HYDROGENATION PLANT YIELDS
(1000 T/D RUBBER)

	Weight % Fresh Feed	Lb/Hr	T/D	B/D	MMSCFD	API Gravity	W % Sulfur
Incoming							
Hydrogen*	0.937	781			3.56		
Rubber	100.000	83,333	1,000				
TOTAL IN	100.937	84,114	1,000		3.56		
Outgoing							
H_2S	0.3	250			0.067		
C_1	0.4	333			0.190		
C_2	0.3	250			0.076		
C_3	1.8	1,500			0.311		
C_4	1.6	1,333		157		111	
C_5-200°F	2.2	1,833		185		76.6	0.51
200-350°F	8.1	6,750		574		44.0	0.54
350-650°F	22.3	18,583		1,315		14.4	0.50
650-975°F	19.337	16,116		1,007		-2.6	0.50
975°F+	7.6	6,333		315		-28.8	0.60
Solids	37.0	30,833	370	---			2.50
TOTAL OUT	100.937	84,114	370	3,553	0.644		

* Hydrogen consumption is 3560 SCF/Ton rubber.

TABLE 40

TABLE 41

HYDROGENATION PLANT MATERIAL BALANCES
(1000 T/D RUBBER)

	Lb/Hr	T/D	B/D	MMSCFD
Incoming Streams				
Hydrogen				
H_2	996			4.542
C_1	419			0.239
	1,415			4.781
Rubber	83,333	1,000		
TOTAL IN	84,748	1,000		4.781
Outgoing Streams				
Gas				
H_2	2.5			0.980
C_1	752			0.429
C_2	250			0.076
C_3	1,500			0.311
C_4	760			0.120
C_5	420			0.053
H_2S	250			0.067
TOTAL OUT	4,147			2.036
Crude Naphtha				
C_4	573		67	
C_5-200°F	1,414		139	
200-350°F	6,750		574	
	8,736		780	
Solids Slurry Product				
Solids	30,833	370		
975°F+	6,333		315	
650-975°F	16,116		1,007	
500-650°F	8,384		573	
	61,666	370	1,895	
Solids-Free Oil				
350-650°F	10,199		742	
	84,748			

V. PRODUCT EVALUATIONS

INTRODUCTION

Evaluation of the carbon blacks produced from both the catalytic and non-catalytic hydrogenation experiments was done by Uniroyal Chemical, a division of Uniroyal, Inc., at their Naugatuck, Connecticut plant. These tests included determining the chemical properties of the carbon black and comparing the physical properties of rubber compounds made using the H-Rubber carbon black products and commercial blacks.

Several types of rubber compounds were formulated for the physical properties testing program. These included a standard test recipe using natural rubber, a standard test recipe using SBR (Styrene-Butadiene Rubber), a modified test recipe using SBR, and a commercial rubber hose recipe. The modified test recipe is considered to be closer to an actual commercial recipe than the standard test recipe, which can be described as a pseudo-ASTM formulation for comparing blacks. In all tests, standard commercial blacks were also compounded for comparisons with the compounds containing HRI produced blacks.

RESULTS

Natural Rubber Compounds

Five compounds were made using natural rubber and H-Rubber carbon black. Only one of these compounds used catalytically produced black, obtained from Period 144-146-1B, while the other four used black from non-catalytic operations. The standard test recipe used to prepare the rubber compounds was as follows:

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Natural Rubber Standard Test Recipe

	Parts by Weight
Natural Rubber	100.0
Stearic Acid	3.0
Zinc Oxide	5.0
MBTS	0.6
Sulfur	2.5
Carbon Black	50.0
	161.1

Three commercial blacks; N-326, N-765, and IRB #3, were used in the standard test recipe for comparison with the rubber compounds containing H-Rubber blacks. Table 42 lists a summary of the properties of both the commercial and HRI produced blacks and the rubber compounds made from them.

The composition of the HRI produced blacks were similar in ash content, 16 to 18 percent, and oil content, 1.3 to 2.7 percent, for both the catalytically and non-catalytically produced blacks. The commercial blacks contained significantly less ash, 0.2 to 0.5 percent, than the H-Rubber product. In the H-Rubber process, the zinc oxide, clay fillers, and other miscellaneous inorganic compounds which are present in a manufactured tire are either not reacted or, perhaps, reduced to sulfide. No attempt was made to separate these materials from the actual carbon black. Although the cure time differed slightly among the various compounds, all compounds were essentially at their ultimate cure when tested.

All the rubber compounds containing H-Rubber blacks exhibited tensile strengths superior to the N-765 semi-reinforcing commercial black, 3230 to 3480 versus 3090, but were slightly inferior to the highly reinforcing N-326 and IRB #3 blacks, with values of 3660 and 3710, respectively. The modulus developed at 300 percent elongation was lower in all cases for the HRI blacks. However, the modulus of 1300 for the compound made with Period 144-150-5B black was similar to the modulus for compounds containing N-326 and N-765 blacks with values of 1575 and 1690, respectively.

EVALUATION OF EXPERIMENTALLY PRODUCED CARBON BLACKS IN NATURAL RUBBER COMPOUNDS

STANDARD TEST RECIPE

	HRI Produced Blacks					Commercial Blacks		
Carbon Black								
Period 144-	146-1B	147-1/2A	147-2B	150-4B	150-5B	N-326	N-765	IRB #3
DBP Absorption, cc/100 Gm	67	67	67	68	66	72	108	73
Ash, W %	16.2	17.1	17.6	18.3	18.1	0.5	0.3	0.2
Oil, W %	1.5	1.3	1.3	2.7	1.9	1.0	0.7	1.0
Carbon Black, W %	82.3	81.6	81.1	79.0	80.0	98.5	99.0	98.8
Rubber Compound								
Cure Time, Minutes	40	40	40	30	30	30	40	30
Cure Temperature, °F	284	284	284	293	293	293	284	293
Tensile Strength, psi	3230	3450	3480	3280	3310	3660	3090	3710
Modulus at 300% Elongation, psi	1050	1060	1050	1095	1300	1575	1690	2270
Elongation, % at Break	560	570	580	550	525	520	490	460
Tear, ppi	340	310	330	310	420	520	400	570

TABLE 42

Elongation of 520 to 580, obtained with compounds containing H-Rubber blacks, compared favorably with the 520 elongation of compounds containing the N-326 black. The tear strengths were generally lower for the compounds containing H-Rubber blacks. However, the compound containing black from Period 144-150-5B operations had a 420 tear strength, which was higher than the 400 obtained with the N-765 intermediate or semi-reinforcing black.

The carbon black produced in Period 144-150-5B compares most favorably with both N-326 highly reinforcing black and N-765 semi-reinforcing black. This run was made using a Kuwait gas oil, having a boiling range of 508°F to 675°F, as slurry oil instead of anthracene oil. The other H-Rubber blacks exhibited good physical properties, but were slightly inferior to this particular black and the commercial blacks tested.

No differences were noted in the gross properties of the carbon blacks produced by catalytic and non-catalytic hydrogenation operations.

SBR Compounds

Standard Test Recipe: Five rubber compounds were made using SBR rubber and H-Rubber blacks in a standard test recipe. Four of these compounds were formulated using carbon black made during non-catalytic operation in Period 144-150-4B and -5B, and Run 144-154. Two different compounds were made from the carbon black from Run 144-154. Both Uniroyal and HRI independently removed the entrained oil from the wet filter cake obtained as the product from the experimental hydrogenation unit. The major difference between the two blacks was that oil content in the Uniroyal extracted black was 2.2 weight percent while that from HRI had 0.4 weight percent.

The fifth compound contained carbon black produced catalytically from tire tread peelings in Run 144-156.

Compounds made from two highly reinforcing commercial blacks, N-326 and IRB #3, were compounded and compared to the compounds containing the H-Rubber blacks. The standard test recipe used for the SBR compounds was as follows:

SBR Standard Test Recipe

	Parts by Weight
SBR	100.00
Stearic Acid	1.50
Zinc Oxide	3.00
Paraflux	6.00
DPG	0.25
DELAC S®	0.85
Sulfur	1.75
Carbon Black	50.00
	163.35

Table 43 lists a summary of the properties of the carbon blacks and SBR rubber compounds made from them.

The ash and oil compositions of the H-Rubber blacks were similar to each other, except for a very low oil content of 0.4 weight percent in one of the Run 144-154 blacks, and a low ash content of 14.7 weight percent and a low oil content of 0.8 weight percent in the black from the tread peelings obtained in Run 144-156.

The same commercial blacks were used as previously reported with the natural rubber compounds. Two compounds using IRB #3, a highly reinforcing black, were made as a check on the reproducibility of the physical testing program.

The results of the tests indicate that the blacks produced in Periods 144-150-4B and -5B have tensile strengths of 3370 and 3190, respectively, which are comparable to values of 3500 and 3710 obtained with IRB #3 commercial black. However, the modulus of 910 and 840 was low compared to 1900 and 2090.

SBR COMPOUNDS

STANDARD TEST RECIPE

		HRI Produced Blacks					Commercial Blacks		
Carbon Black									
Period 144-		150-4B	150-5B	154	154	156[1]	N-326	IRB #3[2]	IRB #3[3]
DBP Absorption, cc/100 Gm		68	66	68	68	----	72	73	73
Ash, W %		18.3	18.1	16.9	17.5	14.7	0.5	0.2	0.2
Oil, W %		2.7	1.9	2.2	0.4	0.8	1.0	1.0	1.0
Carbon Black, W %		79.0	80.0	80.9	82.1	81.0	98.5	98.8	98.8
pH		8.1[4]	7.1[4]	6.6[5]	5.8[5]	----	----	----	----
Rubber Compound	Cure Time, Minutes								
Tensile Strength, psi	30	2370	685	1060	240	1360	370	2325	3235
	60	3490	3220	2220	2490	1965	3710	3425	3765
	120	3370	3190	2140	2740	1975	4090	3710	3500
Modulus @ 300% Elongation, psi	30	385	160	195	75	290	170	675	1365
	60	810	730	515	495	520	890	1595	1925
	120	910	840	550	595	565	1580	1900	2090
Cure Rate, Minutes		----	----	14.0	20.3	16.4	----	----	11.9

1. 144-156 components of carbon black do not add to 100 percent.
2. IRB #3 mixed and cured at same time as 150-4B, 150-5B, and N-326.
3. IRB #3 mixed and cured at same time as both 154 blacks and 156 black.
4. Determined by HRI.
5. Determined by Uniroyal.

TABLE 43

It should be noted, however, that the commercial blacks used in these tests are highly reinforcing blacks producing high tensile strengths and modulus.

The blacks produced non-catalytically in Run 144-154 had a lower tensile strength and modulus than the blacks from Runs 144-150-4B and -5B. It is well-known that acidity retards cure and prevents development of high tensile strengths and modulus. The blacks produced in Run 144-154 were found to be acidic with pH's of 5.8 and 6.6, as compared to the blacks from Periods 144-150-4B and -5B, which had pH's of 8.1 and 7.1. The rubber compounds produced from these acidic blacks also cured slower than the 144-150-4B and -5B rubber compounds.

Good dispersion of the carbon black in the compound is also important in developing high tensile strength and modulus. It was visually observed by Uniroyal that dispersion of the carbon black from Run 144-154 was poor. The reason for this poor dispersion is not known, but it is suspected that there was some residual oil or rubber left on the 144-154 black which caused the poor dispersion and possibly low pH.

Similar results were obtained using the carbon black product from Run 144-156 on tread peelings. It was anticipated that this black should have developed better physical properties than the black produced from whole tires because the black that goes into the tread has different properties than that used in the carcass, but it did not.

Reproducibility of physical property results was observed by comparing the results from the tests on the two IRB #3 compounds. These compounds were made and tested two months apart. Ultimate tensile strength and modulus after 120 minutes were quite similar, though the rate of cure as determined by the development of tensile strength and modulus during the first 30 minutes was quite different.

Modified Test Recipe: A number of rubber compounds were made using a modified test recipe which is a fairly standard recipe throughout the rubber industry. The modified recipe is more like a Uniroyal commercial recipe than the standard test recipe and is cured at 320°F instead of 293°F. In the modified recipe, an aromatic extender oil, Sundex 790 produced by the Sun Oil Company, was used. By comparing the compounds made with the Sundex 790 and commercial black with compounds made with the wet filter cake produced as a primary product by the H-Rubber process, a measure of the value of the unseparated filter cake was obtained.

In other tests in this sequence, H-Rubber gas oil was substituted for Sundex 790 oil and compounded with commercial blacks to evaluate the H-Rubber gas oil as an extender oil.

Table 44 lists a comparison of test results on compounds made with H-Rubber oil and blacks, and Sundex 790 oil. It should be noted that Compounds 6 and 7, formulated using the same recipe, produced significantly different modulus and elongation. Uniroyal has indicated that the results from Compound 7 were more likely to be correct and should be used as the standard commercial compound.

Compound 1 was formulated using wet filter cake containing approximately 45 percent entrained gas oil. This product was not benzene washed, as the blacks used previously were, to remove the entrained oil. Commercial black was added to this compound to achieve a black to oil ratio similar to the standard recipe used for Compound 7. The volume of oil used was also similar in both compounds. Physical property results indicate the rubber compounds to be quite similar. The commercial black developed a higher tensile strength, 1770 versus 1480, but the H-Rubber filter cake mix developed a higher modulus, 950 to 865, and lower percent elongation at break. The ability to use the wet filter cake mix in formulating compounds will save the cost of separating the entrained gas oil from the black.

Compounds 2 and 5 were similar in formulation to Compound 1, but contained a mixture of H-Rubber gas oil and Sundex 790 oil. The carbon black/oil ratios of 1.9 and 1.3 were much lower in Compounds 2 and 5 than the 2.65 used in standard Compound 7. In making these compounds, H-Rubber blacks were used which were not completely extracted and contained 22.6 weight percent oil. For this reason, these results cannot be compared with the standard commercial compound.

SBR COMPOUNDS

MODIFIED TEST RECIPE

	HRI Blacks - Run 144-154					Commercial Blacks	
Modified Test Recipe							
Compound	1	2	3	4	5	6	7
SBR 1500	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Stearic Acid	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Zinc Oxide	3.00	3.00	3.00	3.00	3.00	3.00	3.00
N-774 Black	50.0	----	----	----	----	100.0	100.0
HRI Black/Oil Mix	50.0/37.7	85.2/24.8	----	-----	77.4/22.6	----	----
HRI Black	----	----	100.0	100.0	----	----	----
Sundex 790 (Aromatic Oil)	----	20.0	37.7	37.7	37.7	37.7	37.7
DPG	0.25	0.25	0.25	0.25	0.25	0.25	0.25
DELAC S®	0.85	0.85	0.85	0.85	0.85	0.85	0.85
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75	1.75
Carbon Black/Oil Ratio	2.65	1.90	2.65	2.65	1.3	2.65	2.65
Physical Properties							
Cure Time, Minutes	45	45	30	30	45	45	30
Cure Temperature, °F	320	320	320	320	320	320	320
Tensile Strength, psi	1480	1390	1470	1400	1085	2010	1770
Modulus @ 300% Elongation, psi	950	320	350	320	195	1770	865
Elongation, % at Break	690	855	845	920	980	380	725
Tear, ppi	280	230	230	260	130	250	290

TABLE 44

Compounds 3 and 4 were blended with dry H-Rubber carbon black and Sundex 790 oil. These runs are a direct comparison with commercial Compound 7. As with the standard test recipe previously reported, the dry carbon black from Run 144-154 did not develop tensile and modulus as well as the commercial black. Again, the reasons for the poor physical properties are probably due to poor dispersion of the black in the compound and low pH, which affects the cure rate and, therefore, the ultimate physical properties.

Increasing the pH of the black obtained from Run 144-154 from 5.8 to 8.8 and 9.95 by adjustment with sodium hydroxide and buffering to prevent drift resulted in improved cure rate. Heating the carbon in a nitrogen atmosphere at 500°F for one hour gave similar improvement to that obtained from the pH adjustment in tensile and modulus. These results are summarized in Table 45.

H-Rubber Gas Oil: Table 46 lists the recipes and results for Compounds 8 and 9, which were formulated using commercial black N-774 and H-Rubber gas oil in place of the Sundex 790 gas oil. These compounds are compared with Compound 7, mentioned previously, made with commercial black N-774 and Sundex 790 oil.

Compound 8, made with H-Rubber gas oil extracted by Uniroyal from the wet filter cake, was essentially equivalent to commercial Compound 7 in tensile strength, modulus, elongation and tear.

Compound 9, also made with H-Rubber gas oil obtained as filtrate, did not quite develop the physical properties of Compounds 7 and 8. Based on the poor reproducibility of the commercial test results demonstrated in these tests and previous discussion, the discrepancies between the results of Compounds 8 and 9 may not be significant.

EVALUATION OF MODIFIED CARBON BLACKS IN SBR COMPOUNDS

COMPOUND	AA	BB	CC	DD	EE	FF
STANDARD SBR TEST RECIPE						
SBR 1500	100.0	100.0	100.0	100.0	100.0	100.0
Zinc Oxide	3.0	3.0	3.0	3.0	3.0	3.0
Stearic Acid	1.5	1.5	1.5	1.5	1.5	1.5
Paraflux	5.0	5.0	5.0	5.0	5.0	5.0
IRB #3	50.0	----	----	----	----	----
144-154 Black (As Is - ph = 5.8)	----	50.0	50.0	----	----	----
144-154 Black (pH adjusted to 8.2)	----	----	----	50.0	----	----
144-154 Black (pH adjusted to 9.95)	----	----	----	----	50.0	----
144-154 Black (Heated in N_2 for 1 hour at 500°F)	----	----	----	----	----	50.0
DPG	0.25	0.25	0.25	0.25	0.25	0.25
DELAC® S	0.85	0.85	0.85	0.85	0.85	0.85
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75
DICup 40KE	----	----	----	----	----	----

Mix in Brabender
Mill blend - 2 passes through 0.012" mill
"CC" - 5 passes through hand tight mill

TEST RESULTS

ODR - 320°F (15" preheat - 30' run, 900 cpm 3° arc)						
Viscosity (in. Lbs.)						
Minimum	25.5	20.7	19.3	20.9	21.0	22.6
Maximum	71.4	60.0(e)	54.4(e)	60.9	63.2	67.0(e)
Time (Minutes)						
Scorch	4.9	7.5	8.3	6.2	3.8	6.7
Cure Rate	10.7	20.2	19.9	11.5	9.1	16.7
Physical Properites (Cure 60' at 293°F)						
Tensile (psi)	3500	2530	2000	2700	2850	2850
Elongation (%)	570	850	860	750	720	680
Modulus 300 (psi)	1420	430	390	530	580	790
Shore A	62	56	54	57	59	57

TABLE 45

COMPARISON OF H-RUBBER OIL AND SUNDEX 790 AROMATIC OIL IN SBR COMPOUNDS

	H-Rubber Gas Oil Run 144-154		Commercial Oil
Modified Test Recipe			
Compound	8	9	7
SBR 1500	100.0	100.0	100.0
Stearic Acid	1.50	1.50	1.50
Zinc Oxide	3.00	3.00	3.00
N-774 Black	100.0	100.0	100.0
HRI Oil	37.7	37.7	-----
Sundex 790 (Aromatic Oil)	-----	-----	37.7
DPG	0.25	0.25	0.25
DELAC S®	0.85	0.85	0.85
Sulfur	1.75	1.75	1.75
Actual Loading			
Black (parts by weight)	100.0	100.0	100.0
Oil (parts by weight)	37.7	37.7	37.7
Oil (cc oil/100 Gm rubber)	34.6	35.4	38.4
Physical Properties			
Cure Time, Minutes	30	30	30
Cure Temperature, °F	320	320	320
Tensile Strength, psi	1680	1375	1770
Modulus @ 300% Elongation, psi	940	615	865
Elongation, % at Break	675	840	725
Tear, ppi	270	270	290

TABLE 46

Rubber Hose Compounds

Three compounds were formulated using H-Rubber wet filter cake containing 45 weight percent oil in an EPDM commercial hose compound recipe. A standard recipe was mixed using a commercial black for comparison. The results of these tests are listed in Table 47.

Compounds 10 and 12, using the H-Rubber wet filter cake, differed only in the type of commercial blacks added. In Compound 10, 110.0 parts by weight of N-990 black was added and, in Compound 12, 50.0 and 60.0 parts by weight of N-990 and N-550 blacks were added, respectively. The objective of adding the commercial blacks to the H-Rubber wet filter cake was to achieve the same black/oil weight ratio as in the Commercial Compound 13. No account was taken of the difference in specific gravities between the commercial naphthenic oil (18.2°API) and the H-Rubber gas oil (1.4°API). A comparison of the physical properties of Compounds 10 and 12 with commercial Compound 13 indicates that the H-Rubber wet filter cake will not develop good physical properties in this particular recipe. No tests were performed on H-Rubber dry filter cake with the gas oil removed and compounded with naphthenic oil.

In Compound 11, no zinc oxide was added to the formulation resulting in a rubber product that did not cure. This demonstrates that the zinc compounds in the H-Rubber carbon black do not act as activators.

DISCUSSION OF RESULTS

These results indicated that the H-Rubber gas oil and carbon black products can be utilized in making commercial rubber products.

It appears from the data that use of the H-Rubber gas oil in compounds can produce essentially the same physical properties as compounds made by using commercially available oils. One deficiency in the gas oil is that, because it was produced non-catalytically, the odor is not acceptable. Unfortunately, no compounds

EPDM HOSE COMPOUNDS

EPDM Hose Recipe	Run 144-154			Commercial
Compound	10	11	12	13
Royalene 502®	100.0	100.0	100.0	100.0
Zinc Oxide	5.0	----	5.0	5.0
N-550 Black	----	----	60.0	60.0
N-774 Black	----	----	----	60.0
N-990 Black	110.0	110.0	50.0	150.0
Black/Oil Mix	160.0/120.0	160.0/120.0	160.0/120.0	
Naphthenic Oil	----	----	----	120.0
Stearic Acid	1.0	1.0	1.0	1.0
MBT	0.5	0.5	0.5	0.5
TUEX	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5
Physical Properties				
Cure Time, Minutes	30	30	30	30
Cure Temperature, °F	320	320	320	320
Tensile Strength, psi	690	DID	750	1340
Modulus at 300% Elongation, psi	130	NOT	380	----
Elongation, % at Break	900	CURE	830	280

TABLE 47

were prepared from gas oils which were made catalytically or from hydrotreated gas oils made initially non-catalytically. Both of these products have a much better odor.

The data on compounds produced from the H-Rubber carbon black is not as clear. Most of the compounds made were characterized by slow cure rate and low modulus. One important exception was Compound 1, where a blend of virgin carbon black and wet filter cake gave satisfactory results. This may indicate that some of the experimental procedures used to extract and dry the carbon black contained in the filter cake may have caused some changes in its properties. For example, some oily residue left on the carbon black may seriously impair its dispersion in the rubber compound.

Although some uncertainty exists at this time, it appears that the carbon can be reused. It could most probably be used in place of FEF, SRF, HMF, and GPF blacks. The production of these blacks was 976-million pounds in 1968. One 1,000 ton per day H-Rubber plant would produce 244-million pounds of carbon black product per year.

VI. ECONOMIC CONSIDERATIONS OF THE H-RUBBER PROCESS

PLANT LOCATION CONCEPTS

The overall economics for the H-Rubber process depend primarily on the price that the plant must pay for collecting and grinding tires, the cost of the hydrogenation operation, and the value of the carbon black and liquid products produced. It is obvious then that the most optimistic set of circumstances would be for the plant to be close to a metropolitan area adjacent to an oil refinery, and close to major users of carbon black to minimize the transportation costs for this product.

Recently, it has been estimated that the costs for collecting and transporting used tires are in the range of $9 to $20 per ton, depending on geography and distance[14]. A compact metropolitan area would offer the lowest potential cost for a tire disposal operation.

Locating the refinery adjacent to an existing petroleum refinery could provide hydrogen, steam, electricity, water, fuel gas, boiler feed water, maintenance services, pollution control facilities, and management assistance at incremental costs rather than at the higher costs necessary for an independent facility. In addition, the refinery could serve as a convenient outlet for the liquid and gas products made in the H-Rubber process. The approximately 3,000 barrels per day of liquid products would represent a very small percentage of the output of a large modern United States refinery. These plants process on the order of 100,000 to 400,000 barrels of crude per day.

Minimumization of carbon product transportation costs are an obvious incentive to plant profitability.

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Although all three aspects must be considered in locating the plant, it would appear that the tire collection costs would be the dominant factor.

PLANT SIZE

A recent Environmental Protection Agency report[13] gave a geographical distribution of the generation rates of used tires. This data was used to prepare Table 48, which summarizes the most likely locations for commercial H-Rubber plants. The areas listed would provide tires for H-Rubber plants ranging from 150 tons per day to 950 tons per day. There are ten locations in the 150 to 250 ton per day range, three in the 350 to 500 ton per day range, and one at 950 tons daily.

There are existing refineries located within all the areas cited.

ECONOMIC ANALYSIS OF A 1,000 TPSD H-RUBBER PLANT

Table 49 presents a summary of the overall H-Rubber process economics. Carbon product was valued at $0.06 per pound, liquid product at $3 per barrel, and -24 mesh ground rubber feed at $30 per ton. With a total H-Rubber plant cost of $9.47 million, including offsites, a payout, based on profit, of 3.92 years is anticipated. This period is based on six percent interest on working capital and fifteen year straight line depreciation.

POTENTIAL LOCATIONS FOR H-RUBBER PLANTS

Metropolitan Areas of 100 Mile Radii	Estimated Plant Size, Ton/Day
New York/Philadelphia/Baltimore	950
Chicago	350
Los Angeles	550
Miami	250
Detroit	250
Louisville	250
Boston	400
San Francisco	250
Minneapolis/Saint Paul	100
Saint Louis	150
Buffalo	150
Dallas/Fort Worth	150
Houston	150
Atlanta	150

TABLE 48

TABLE 49

ECONOMIC SUMMARY FOR 1000 TPSD PLANT

Plant Investment, $/Millions

On-Site	8.429
Off-Site	1.041
	9.470
Working Capital	1.850

	Unit Prices	Annual $ Millions	$/Ton Rubber
Revenue			
Carbon	$0.06/Lb	14.652	44.40
Naphtha	$3.00/Bbl	0.772	2.34
Gas Oil	$3.00/Bbl	2.611	7.91
Fuel Gas	$0.40/MMBTU	0.277	0.84
TOTAL REVENUE		18.312	55.49
Expenses			
Ground Rubber*	$30/Ton	9.900	30.00
Electricity	$0.008/KWH	0.167	0.51
Fuel Gas	$0.40/MMBTU	0.795	2.41
Cooling Water	$0.05/M Gal.	0.202	0.61
Boiler Feed Water	$0.10/M Gal.	0.002	0.01
Hydrogen	$0.50/MSCF	0.749	2.27
Operating & Management Payroll		0.284	0.86
Overhead (100% Payroll)		0.284	0.86
Maintenance at 4% On-Site Investment		0.337	1.02
Maintenance at 2% Off-Site Investment		0.021	0.06
Insurance & Taxes at 2% Total Investment		0.189	0.57
Interest on Working Capital at 6%		0.111	0.34
Depreciation, 15-year Straight Line		0.631	1.91
TOTAL EXPENSES		13.672	41.43
PROFIT BEFORE TAXES		4.640	14.06
PROFIT AFTER TAXES AT 48%		2.413	7.31
% RETURN ON INVESTMENT AS PROFIT		25.5	
PAYOUT, YEARS		3.92	

* Total Cost, including collection

Ground Rubber Costs

In order to simplify the economic analysis, ground rubber was treated as a feed commodity available at a predetermined price. This was done to permit a clearer understanding of the relation of the H-Rubber part of the scheme to the overall economics. The value of $30 per ton for -24 mesh ground rubber includes the cost of collecting. As previously noted, collection costs have been estimated to be in the $9 to $20 per ton range. If we can assume that, in a metropolitan area with a concentrated population and highly developed transportation network, that the lower range costs could apply, $10 per ton would appear to be a conservative cost for collection.

Uniroyal has prepared analogous capital costs and operating cost estimates for a plant grinding 1,000 tons per day of used rubber tires and producing one-quarter-inch ground rubber with fiber or -24 mesh ground rubber without fiber. For the larger particle size product, a plant costing $7.2 million is required, while for the smaller product, the plant cost rises to $21.7 million. Based on capital recovery, including seven percent interest, useful lives of 16 years for land improvements and utilities, 20 years for buildings and 12.5 years for machinery and equipment, the annual processing costs are $3.2 million and $6.4 million for the larger and smaller products, respectively. Using these costs and assuming 330 days per year of operation, the total costs for grinding, including return on investment, would be $10 per ton for one-quarter-inch product and $20 per ton for -24 mesh product.

On the basis of this information, a total cost of $30 per ton for -24 mesh fiber free ground rubber, $10 for collection and $20 for grinding, was conservative. This cost would be reduced if the collection system were changed so that waste tires could be delivered by a municipality to a grinding plant at no charge to that plant. This could be justified on the basis that normal present-day practices for waste tire disposal are unsatisfactory.

If the H-Rubber process could accept one-quarter-inch particles as feed, then the grinding costs could be reduced from $20 to $10 per ton. This alone would significantly improve plant

payout time.

Improved grinding technology for used rubber tires is the third area where significant cost reductions could be made. Present-day technology would require about 70 people for a 1,000 ton per day grinding plant. This is compared to normal chemical and petroleum refinery operations processing this amount of feed. In addition, maintenance costs for grinding roll wear and replacement are high.

Carbon Black Value

The precise value of the carbon black produced has not been established as yet. Results from attempts to compare its properties to standard blacks in standard test recipes have been variable. It appears that some of the deficiencies noted earlier in the rate of curing, or the modulus of elasticity at 300 percent elongation are related to contaminants on the surface of the carbon. Improvements in the separation procedure may be required to better evaluate the carbon. Poor dispersability of the carbon in rubber samples was only noted in those samples from which the H-Rubber product oil was removed. This obviously indicates that the benzene solvent used to remove the oil caused some other reaction which made dispersion difficult. Other requirements for pH adjustment and carbon pretreatment have not been fully evaluated.

In spite of these difficulties in evaluation, which are typical of the problems of working with a new and somewhat different material, it is felt that the carbon recovered will be useful either as a blend component with, or a replacement for, FEF, SRF, HMF, and GPF blacks. These blacks are currently sold for $0.06 to $0.07 per pound and their total production was 976 million pounds in 1968. One 1,000 ton per day H-Rubber plant would produce 244 million pounds of carbon black product per year.

If tread peelings, which contain higher structure and, therefore, more valuable blacks, could be processed in blocked operation, it might be possible to increase the value of a fraction of the

product to about $0.08 per pound. This would be offset by the higher costs involved in separating the tread from the rest of the tire, storing it, and processing it later through the H-Rubber plant.

No estimates have been made on any potential alternate uses for the carbon since the largest use for carbon black in this country is for tires. If the properties of the carbon are not satisfactory for use in tires, there is always the possibility that other rubber products, such as automotive mats, hose, or semi-pneumatic tires, could provide a means of using the carbon.

H-Rubber Plant

The total plant investment for a 1,000 ton per day H-Rubber plant was estimated at $9,470,000 for 1972 costs. It is felt that this number is quite reliable since it was based on costs for similar ebullated bed hydrogenation units built during the last several years. The estimates have been updated frequently. A breakdown of these costs in terms of equipment, materials, erection, and others is presented in Table 50. The flow sheet for this plant was presented and described earlier in Section IV.

The H-Rubber plant cited was designed to produce a mixture of carbon black and recyclable oil for tire manufacturing. No physical separation step for carbon and oil was included, other than distillation to remove most of the slurry oil. As was noted earlier, no dispersion problems were encountered using unseparated H-Rubber product mixtures of carbon black and oil.

Table 51 summarizes the capital investments, products, raw materials, and utility requirements. Table 52 summarizes the operating and management payroll for the H-Rubber plant.

Inherent in the development of these economics has been the assumption that the H-Rubber plant would be located adjacent to an existing petroleum refinery. The advantages to the H-Rubber plant are numerous. For example, the refinery could provide electricity, cooling water, boiler feed water, sweetened fuel gas, and hydrogen

TABLE 50

1,000 TON/DAY H-RUBBER PLANT

ESTIMATED CAPITAL INVESTMENT

Major Equipment		
Pumps	$ 491,000	
Reactor	400,000	
Heaters	548,000	
Exchangers	577,000	
Towers	95,000	
Drums	91,000	
Compressors	425,000	
	$2,627,000	$2,627,000
Total Materials		
Foundations, Structural Steel, Valving, Piping, Electrical, Insulation, Instruments	$1,769,000	4,396,000
Erection	2,198,000	
Spare Parts	176,000	
Freight and Insurance	176,000	
	$2,550,000	6,946,000
Engineering	700,000	7,646,000
Contingency at 5%	382,000	8,028,000
Fee at 5%	401,000	
TOTAL ON-SITE INVESTMENTS		$8,429,000
Off-Sites		
Utilities	$ 490,000	
Buildings	91,000	
Tankage	460,000	
	$1,041,000	
TOTAL OFF-SITE INVESTMENTS		$1,041,000

TABLE 51

1,000 TON/DAY H-RUBBER PLANT

SUMMARY OF CAPITAL INVESTMENT, PRODUCTS, RAW MATERIALS AND UTILITIES

Capital Investment	
On-Site	$8,429,000
Off-Site	1,041,000
	$9,470,000
Products	
Carbon, TPSD	370
Naphtha, BPSD	780
Gas Oil, BPSD	2637
Sulfur Free Gas (NHV - 1065 BTU/SCF), MMSCFD	1.969
Raw Materials	
Ground Rubber, TPSD	1000
Hydrogen (95% Purity), MMSCFD	4.542
Utilities	
Electricity, KWH	2640
Fuel, MMBTU/Hr	251
Cooling Water, GPM	8520
Boiler Feed Water, GPM	32

TABLE 52

1,000 TON/DAY H-RUBBER PLANT

OPERATING AND MANAGEMENT PAYROLL

	Men/Shift	Total Men On Payroll
Operators	4	17
Shift Foreman	1	4
Vacations, Sick, Replacements		2
TOTAL		23
Operators and Foreman for Plant Operations		23
Average Hours Worked Per Year, Hrs/Man		1900
Average Pay, $/Hr.		5.00
Operating Payroll (23), (1900), ($5.00)		$218,500
Supervision, Management, Etc. at 30% of Operating Payroll		65,500
TOTAL OPERATING PAYROLL		$284,000

to the rubber plant at incremental costs. This would serve to substantially reduce H-Rubber plant operating costs since a large refinery produces or purchases these utilities at minimum cost because of the scale of operation. In addition, the liquid and gas products from the H-Rubber plant could be sold to the refinery as is and upgraded if required in large scale equipment for which they would be an incremental amount of feed. This would eliminate a marketing function at the H-Rubber plant which would be costly because of its small size. As another example of the advantageous relationship that would be possible, the 2,000,000 SCFD of refinery gas produced could be more economically sweetened in the existing refinery equipment rather than in new independent equipment.

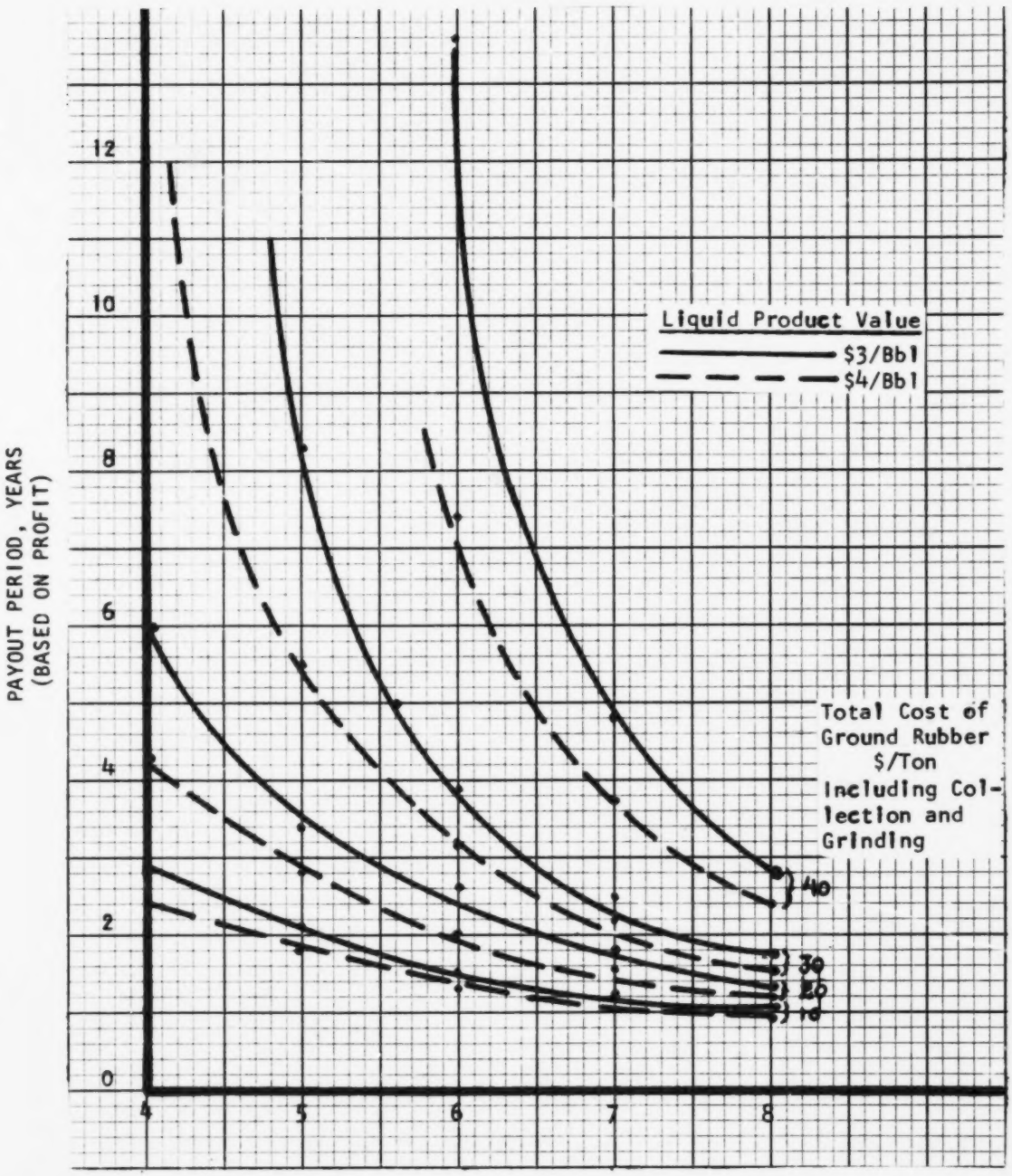
H-RUBBER PLANT PROFITABILITY

The sensitivity of H-Rubber plant economics to carbon value, liquid product value, and the total cost of ground rubber is presented in Figure 7. Payout periods were calculated for ground rubber prices of $10, $20, $30 and $40 per ton, liquid products of $3 and $4 per barrel and carbon prices between $0.04 and $0.08 per pound. It appears that product carbon prices below $0.05 per pound would require ground rubber feed at no more than $20 to $25 per ton to maintain plant payout at less than five years. Carbon prices of $0.06 per pound would allow rubber prices up to somewhat more than $30 per ton. If ground rubber costs amounted to $40 per ton, a product price of $0.07 per pound would be required.

FIGURE 7

EFFECT OF CARBON VALUE, LIQUID PRODUCT VALUE

AND GROUND RUBBER COST ON PAYOUT PERIOD



APPENDIX

DEVELOPMENT OF ANALYTICAL AND EXPERIMENTAL TECHNIQUES

ANALYTICAL TEST DEVELOPMENT

Technique for Separation of Catalyst from Carbon Black Products for Stirred Autoclave Runs

The technique for the separation of catalyst from the carbon black product was improved after stirred autoclave Runs 193-140 and -144. For both these runs, the liquid-solids product was benzene extracted to separate the solids (catalyst, carbon black, and inorganics) from the oil. The catalyst was separated from the carbon black by screening. The screening of the catalyst from the carbon black product was unsuccessful because the catalyst was quite broken up during these runs. In Run 193-140, a high stirrer speed (750 rpm) was used; Run 193-144 lasted six hours (200 rpm), resulting in extensive catalyst breakup.

For the remaining runs, the catalyst breakup was kept to a minimum by using a 200 rpm stirrer speed and limiting runs to two hours in length. The technique for separation for Runs 193-145 to -149 consisted of washing the total liquid-solids product with benzene through a 60 mesh screen to remove the catalyst. A benzene extraction was done on the remaining oil-carbon black product to separate out the carbon black. The benzene-oil mixture was then separated by distillation.

Because of the excessive length of time employed in the benzene extraction step, pressure filtration was used in runs after Run 193-149. The pressure filtration preceded the benzene extraction

step in the separation process to cut down on the length of time it took to extract the cake. Pressure filtration left 13 weight percent oil in the black and, therefore, could not be used as a complete replacement for the benzene extraction step.

The overall separation procedure used for all stirred autoclave runs after Run 193-149 consisted of the following:

(1) Separation of catalyst from oil-carbon black mixture by 60 mesh screen.

(2) Benzene extraction of catalyst left on the screen.

(3) Pressure filtration of oil-carbon black mixture.

(4) Extraction of carbon black cake with benzene.

(5) Separation of benzene from product oil by distillation.

(6) Drying of carbon black filter cake.

Pseudo-Dibutyl Phthalate Number Determinations

Determination of carbon black structure as a means of evaluating the screening runs was investigated. The standard ASTM method involves titration of the carbon black with dibutyl phthalate in a mixing chamber with a constant speed rotor. The end point is a preselected torque and a torque sensing device shuts off the buret automatically when the mixture begins to gel.

The instrument used for this ASTM determination is called the Cabot Absorptometer and is available from Brabender Instruments for approximately $2,300 ($1,400 without the constant rate buret).

Titration with DBP was attempted on Uniroyal and Continental Carbon calibration blacks with the hope that the end points

could be visually determined, eliminating the need for special ASTM approved equipment.

The following table lists a comparison of DBP numbers of calibration blacks versus DBP numbers determined by titration at HRI. This data is plotted in Figure 8.

Calibration Black	Standard DBP Number	HRI Lab DBP Number
Continental Carbon	67.3	67.3
	81.8	81.0
	87.1	88.3
	99.5	99.0
	120.8	121.0
	135.2	135.0
Uniroyal	106.9	104/105

From these data, it is evident that visual determination of the end point of the DBP titration gives a reliable method of screening runs with regard to the quality of the carbon black structure. These visually determined DBP numbers are referred to as pseudo-DBP numbers in this report.

Investigations of the effect of the physical and chemical treatment of carbon black products on pseudo-DBP numbers was checked.

Two standard carbon blacks, whose standard DBP numbers could be reproduced by the HRI Analytical Lab, were subjected to benzene extraction and pressure filtration with benzene. Pseudo-DBP numbers were determined and are compared in the following table.

Standard	Benzene Extracted Pseudo-DBP	Pressure Filtered with Benzene Pseudo-DBP	No Treatment	
			HRI Pseudo-DBP	Standard DBP
Jug #1	62.3	61.6	67.3	67.3
4B	106.0	105.0	99.0	99.5

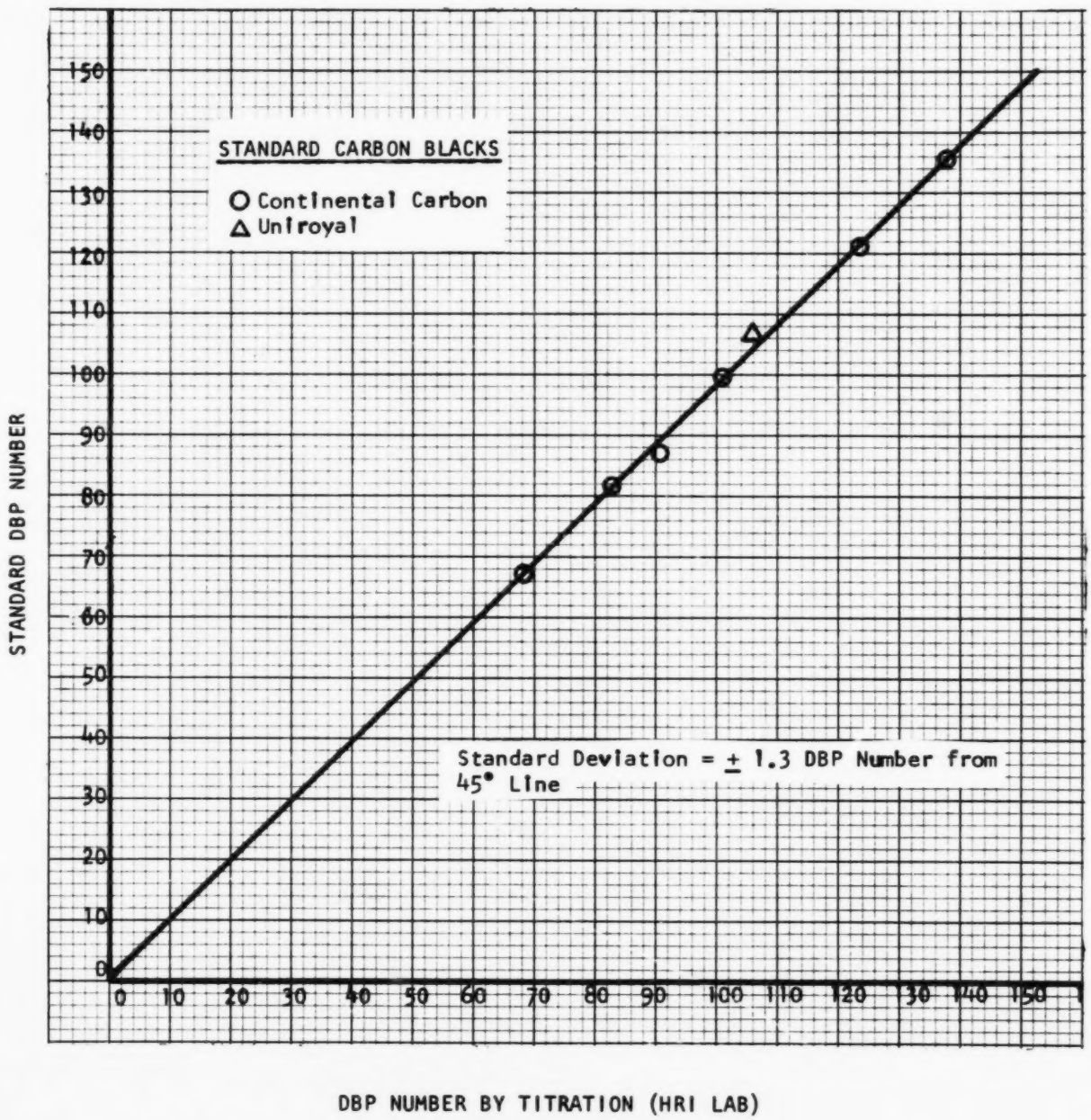
FIGURE 8

COMPARISON:

STANDARD DBP NUMBER

VERSUS

DBP NUMBER BY HRI TITRATION



Treatment of the carbon black obviously changed the DBP number though benzene extraction and pressure filtration with benzene both gave the same results. This would indicate that entrained benzene has somehow affected the results.

All pseudo-DBP determinations in this report were made on benzene extracted carbon black. These DBP numbers are, therefore, not true values, but are affected by the benzene as shown above. They did, however, give adequate results for our objectives.

A comparison of Uniroyal determined DBP numbers using the ASTM method versus HRI pseudo-DBP numbers is listed below. The titrations were performed on HRI produced carbon blacks.

Run	Pseudo-DBP Number	Uniroyal ASTM DBP Number
144-146-1B	66/69/72	67
144-147-1, 2A	65	67
144-147-2B	67/67	67
144-150-4B	68	68
144-150-5B	65	66

The comparison is excellent and shows that the HRI pseudo-DBP method is adequate for determining the quality of the carbon black structure.

SLURRY PUMPING TESTS

Preliminary static settling tests were made on rubber slurries to determine the amount of dilution needed for good fluid characteristics. At 15 weight percent rubber in anthracene oil, a sort of gel was formed, indicating the slurry might be too thick to pump. At 10 weight percent rubber, the rubber particles settled out with a continuous liquid phase present. This type of slurry can usually be pumped.

Rubber pumping tests were conducted in a modified ebullated bed pilot plant unit in which the reactor was bypassed. Slurries of rubber and anthracene oil were pumped from a charge pot to a high pressure receiver held at 1,000 psig. The feed system consisted of a charge pot with a centrifugal pump for recycle mixing and a positive displacement pump to feed the solution to the receiver.

An 18 weight percent rubber-in-anthracene solution was pumped for two hours with no problems. Throughput was approximately 2,300 Gm/Hr (500 Gm/Hr of rubber). This result is in contrast to the static results mentioned above and probably indicates that some mechanical breakdown of the rubber occurred in passing through the low pressure pumping circuit. It is possible to pump a higher concentration of solids if the average particle size is reduced.

A 20 weight percent solution was pumped for one hour, but difficulty in maintaining the recycle flow was encountered. The recycle flow was sporadic for most of the hou and stopped completely near the end of the hour. Anthracene oil was added to the charge pot to initiate recycle flow again.

During the process development runs, in which rubber was actually reacted, it was found that pumping slurries containing greater than 15 weight percent rubber for long periods of time was difficult. The suction line to the charge pump and the charge pump checks often plugged up with rubber.

FIBER SEPARATION BY ELUTRIATION AND SCREENING

Fibers at concentration from two to four weight percent were present in the ground rubber tire feed received from Uniroyal Chemical. In operating the continuous bench-scale units, it was found that the glass fibers "matted" together and plugged the catalyst bed, while the fibers, such as nylon, polyester, and rayon, were reacted to gas and liquid products.

In an effort to remove all the fibers to prevent problems caused by the glass fibers, the rubber feed was pretreated by nitrogen elutriation and by screening.

The elutriation system consisted of a two-inch diameter lucite tube opened at the top. Nitrogen, controlled by a rotameter, was injected into the bottom of the tube at rates which carried the fibers out the top of the tube and left the rubber in the column. The batch operation was continued until no fibers were visible at the top of the column. It is estimated that about 50 to 75 percent of the fine fibers were removed from the rubber.

The second method used to separate the fibers from the rubber was screening the rubber through a vibrating 36 mesh screen. A large percentage of the fibers balled up on the top of the screen and were removed with the +36 mesh rubber.

Neither method was successful in removing enough fibers to ensure free flow of the glass fibers through the catalyst bed, but the amount of time on stream before reactor plugging occurred improved slightly.

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